IMPERIAL AGRICULTURAL
RESEARCH INSTITUTE, NEW DELHI.

THE ANALYST

THE ORGAN OF THE

Society of Public Analysts and other Analytical Chemists

A MONTHLY JOURNAL DEVOTED TO THE ADVANCEMENT
OF ANALYTICAL CHEMISTRY

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VOL. LVII

PUBLISHED FOR THE SOCIETY BY
W. HEFFER & SONS LTD.
4, PETTY CURY, CAMBRIDGE, ENGLAND
1932

Errata

Vol. LVII. 1932.

P. 337, line 23, *for* "69·30" *read* "3·465."

P. 377, third column of first table, *for* "Average error per cent." *read* "Average error per cent. in reading."

P. 570, line 20, *for* "Gallenkamp" *read* "Baird and Tatlock."

P. 571, line 7 from the bottom, *for* "acidity of" *read* "acidity and."

Milk Products Sub-Committee Report, No. 3.

P. 650, line 3 from bottom. Add to the reagents required: "2 *N* sodium hydroxide solution (approximate)."

P. 651. *For* "add *N*/2 sodium hydroxide solution" *read* "add the 2 *N* and, towards completion, *N*/2 sodium hydroxide solution."

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  in impregnated wood; Determination of ——. 737.
  in water supplies. E. Bartow and O. M. Weigle, 401.
  Rinnmann's green test for ——. A. A. Benedetti-Pichler, 673.
  Separation of tin from —— by means of sodium hydrosulphite. B. S. Evans, 362.
Zinc Oxide: Use of —— in determining cobalt manganese. J. I. Hoffman, 272.
Zirconium: Quantitative separation of tantalum, niobium, titanium and ——, and a new analytical grouping. W. R. Schoeller and A. R. Powell, 550.

PRINTED BY W. HEFFER & SONS LTD., CAMBRIDGE, ENGLAND.

JANUARY, 1932 Vol. LVII., No. 670

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, December 2nd, the President, Dr. J. T. Dunn, being in the chair.

Certificates were read for the first time in favour of:—Albert Green, M.C., M.Sc., Ph.D., F.I.C., John Farrar Hardwick, B.Sc., A.I.C., Ernest Stephen Hawkins, B.Sc., A.R.C.S., F.I.C., Joseph Robert Johnson, F.I.C., M.Inst.M.M., Arthur Pillans Laurie, M.A., D.Sc., F.R.S.E., and John Morgan Tucker, B.Sc., A.I.C.

Certificates were read for the second time in favour of:—Thomas Whittaker Lovett and William Charles Alfred Wise, B.Sc.

The following were elected Members of the Society:—Charles Hubert Francis Fuller, B.Sc., F.I.C., Ganesh Chandra Moitra, B.Sc., Eric Charles Wood, B.Sc., A.R.C.S., and Robinson Pearson Wood.

The following papers were read and discussed:—"A Micro-method for the Determination of Uronic Anhydride Groups in Pectic Substances," by H. W. Buston, Ph.D., D.I.C.; "The Composition of Linseed Oil," by N. E. Cocchinaras, Ph.D.; "Oil from Malayan *Aleurites Montana* and the Properties of Hong Kong Oil," by T. Hedley Barry; and "The Calcium Fluoride Method for the Determination of Fluoride, with Special Reference to the Analysis of Nickel Plating Solutions," by S. G. Clarke, Ph.D., A.I.C., and W. N. Bradshaw, B.Sc.

NORTH OF ENGLAND SECTION

A meeting of the Section was held in Leeds on December 5th, 1931. There were 28 present, and the Chairman (Mr. C. J. H. Stock) presided.

Dr. Dunn, President of the Society, read a paper on "The Public Analyst and his Professional Relationships," in which he stated clearly the principles which he suggested a Public Analyst should maintain, drawing illustrations from his own personal experience. Many members took part in the discussion which followed.

A resolution of sympathy was passed with the relatives of the late Mr. W. Foulkes Lowe.

The Identification of Wood and Wood Charcoal Fragments

BY J. CECIL MABY, B.Sc., A.R.C.S.

(*Read at the Meeting, October 7th,* 1931)

INTRODUCTION.—It is now many years since forest products research, as distinct from the much older science of sylviculture, first began to receive expert attention, and certain common woods to be subjected to anatomical examination;* while, more recently, the physical and chemical properties of wood have been made the subject of special investigations, both in America and in Europe, with an increasing recognition of the enormous value of wood substance, considered either as convertible timber or as a complex of chemical compounds.

The physics and chemistry of wood, however, I shall not discuss in the present paper, my object being briefly to outline the value and importance of a purely anatomical knowledge of the many thousands of commercial woods which have been, and are still, used throughout the world for constructional purposes, cabinet work and the manufacture of innumerable articles of everyday utility.

As is well known to microscopists, each kind of wood possesses its own specific structure and physical properties, the knowledge of which, from originally being a matter of purely botanical significance, was quickly seen to be also of considerable economic and forensic importance.

Thus it was thought possible, by determining the average range of structure and percentage amounts of the various elements in a number of samples belonging to a given commercial species, to deduce therefrom certain *standards* of wood structure for the species, as also in relation to particular purposes and industries. Such standards are still in the process of being worked† out, with an ultimate intention, first, of enabling the selection of the best type and quality of wood for a given purpose; and second, so that sylviculturalists may know more certainly what types of timber are required of them, and how to grow such timber most economically.

Moreover, it has been found that detailed knowledge of the specific structure of commercial woods renders possible the identification of quite minute samples of unknown timber. That such identifications may frequently be of value in commerce, in archaeology, and for forensic purposes, will be easily appreciated. Indeed, in the few years since the inauguration of the two principal institutes in this country,‡ many hundreds of crucial identifications have already been carried out for firms and individuals. For instance, a company may purchase a large consignment of timber purporting to be mahogany, or American white oak, say; whereas the consignments may be found by the technologist to be no better than a cheaper and poorer substitute for mahogany (a name often used extremely loosely, since the world's resources of true mahogany have been practically depleted), and, in the second place, American swamp oak—an almost useless timber which, for some undetermined physico-chemical reason, is liable to extreme "collapse"* on seasoning.

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* *Vide*, for example, the work of Robert Hartig in Germany, upon beech and oak, towards the end of the last century.

† Such investigations are being made in this country upon common ash, elm and oak, in the last of which I have been engaged.

‡ The Forest Products Research Laboratory (D.S.I.R.), Princes Risborough, Bucks., and the Imperial Forestry Institute, Oxford.

Again, pieces of wood and wood charcoal from fallen, burnt and buried edifices, the handles of ancient implements, portions of inhumated and fossilised trees, etc., are constantly requiring identification in order to prove some legal point, to help the antiquarian to solve his historical problems, or to extend our botanical knowledge of the past flora of a country or district.

Not a year passes but many interesting archaeological finds are made in this country alone of charcoals and wood fragments: portions of charred beams and posts, the remains of stockades, piles from lake dwellings, spear hafts, implement handles, charcoals from ancient hearths and furnaces—one and all can be identified. I have, personally, been fortunate in receiving many such remains for examination during the past few years, and can say at once that the instances are few in which interesting information is not thereby acquired. For example, it has been possible to show that red oakwood—presumably *Quercus cerris*—was used in an Elizabethan glass furnace at Hambledon, Surrey, although the tree was not previously supposed to have been introduced until about 1735; while the existence of beech in south-west England long before Roman times has been corroborated by several discoveries, running back to early Neolithic times. In other cases, it has been possible, from the species and apparent sizes of wood employed, to confirm the hypotheses of the excavators as to the nature of the structures in question. Other interesting facts also appear, such as the use of a seemingly Indian wood in a Roman spear-haft found near St. Albans, and the occurrence of now exotic timbers in certain ancient Egyptian structures.

THE PREPARATION OF MATERIAL.—The mode of preparation of material for microscopic examination will depend chiefly upon its physical condition, this being determined by its past history. If it is thought necessary to section a specimen, either for purposes of detailed investigation or for photomicrography and record, the preliminary treatment may then be relatively long and delicate. Often, however—especially with the better-known woods—it is unnecessary for an experienced wood technologist to cut sections at all, a superficial view, obtainable by means of a good hand-lens or low-power binocular microscope, frequently being sufficient to permit of identification. In fact, I have generally found that wood charcoals may best be broken across by hand, to show a clean, clear cross-section of the grain (the most useful view). Practically as much is thus seen superficially as in a thin microscopic section made from embedded material, for the intense blackness of the tissues often renders the more minute structures (*e.g.* pitting of the cell walls) invisible by transmitted light.

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* "Collapse" is a remarkable form of distortion and exaggerated shrinkage occurring in certain timbers during seasoning. The phenomenon, which is not to be confused with warping or irregular shrinkage proper, is found to result from an actual collapse of the cell walls—worse in some parts than in others.

An average charcoal sample—even after three or four thousand years under ground—normally preserves every main detail of the wood structure in wonderful perfection, whereas uncharred and sodden wood is frequently found to have suffered considerable internal decay and dissolution, often accompanied by extreme compression and "collapse." Hence, unless the specimens have become partly vitrified or "coaly" (reason unknown) as does sometimes happen, charcoals may usually be said to present better material for identification than excavated wood. Rarely, however, charcoal fragments are dug up in so damp and crumbly a condition that no kind of treatment may avail to preserve their form for microscopic examination. Such specimens are not brittle enough to be broken across, as described above, and they will not always stand slow oven-drying or treatment with alcohol, previous to embedding. The only other alternative seems to be very slow drying in a desiccator, employing hygroscopic salts. But even then the specimens might break up when dropped into the solvent spirit for embedding. This I have not yet attempted.

Very rotten wood samples, as well as charcoals, may also be examined superficially, by breaking across the grain—*never* by cutting, even with the sharpest razor; an alternative method is that of careful impregnation with wax or celloidin, as described below.

In making superficial examinations, whether of wood or charcoal, whereof sufficient detail can thus be observed, a hand lens, though useful, is uncertain and trying to the eyes. A good, low-power binocular microscope, magnifying X 20–30 lin., and having a large field of view (*e.g.* not less than 25 sq. mm.), is, therefore, almost indispensable. The only other, and critical factor, as I need scarcely mention, is the incidence and intensity of illumination.

So far, I have spoken only of superficial examination. Material should, however, be classified as normally requiring one of four kinds of preliminary preparation, according to circumstances. Wood that can be sectioned in a microtome, without preliminary treatment of any kind, must have been wet-rotted in an unusual manner, and is but rarely met with. Even so, the preliminary infiltration of some binding substance is highly desirable.

These four treatments, of which the first two have already been considered, are as follows:—

(1)	Brittle specimens of coarse texture or familiar structure.	Break sharply across the grain, in the hand, cleave longitudinally (not cut), and examine superficially.
(2)	Tough wood specimens of relatively coarse texture or familiar structure.	Cut transversely with a sharp knife, cleave longitudinally (not cut), and examine superficially.
(3)	Normal, tough specimens of wood, whether ancient or modern, of fine texture or unfamiliar structure.	First soften by boiling in water or by treatment with hydrofluoric acid, or both, followed by pickling in glycerin and alcohol. Section on a microtome.
(4)	Specimens of fine texture, unfamiliar charcoals, and rotten or crumbling specimens of wood or charcoal.	Embed in either paraffin wax or celloidin, according to relative hardness, and section with a microtome for detailed examination.

With regard to the third group, ordinary wood samples may be said to be either very hard, hard, medium or soft; the first three types are capable of blunting a good steel knife too quickly to enable large thin sections to be cut for microscopic purposes, until the siliceous skeleton, which pervades the entire cellular meshwork, has first been dissolved away by means of hydrofluoric acid. Common oak, for instance, may be classed as "medium to hard," whilst most tropical woods are "very hard." Coniferous timbers, on the other hand, are usually soft enough to cut well after 5 to 10 hours' boiling in water and some storage in a mixture (50:50) of methyl alcohol and glycerin, lasting, say, from a week to twelve months. But the latter solution, being used largely for storage purposes, may, when time is short, be omitted. Moreover, as is well known, glycerin has a softening action upon many organic tissues, and alcohol eventually spoils staining properties; so that storage in this solution can be over-prolonged.

It is usual, therefore, to give the hard woods a treatment of one to four weeks in hydrofluoric acid, diluted down to about 50 per cent. with water, in accordance with the relative hardness of the wood, and to keep the material in hard rubber bottles; this step can be omitted with soft woods. The acid, of course, must be thoroughly washed out before transferring the material to 95 per cent. alcohol, and, finally, to the alcohol-glycerin storage mixture.

Some woods possess sufficient natural colour not to require staining, but wood sections may be suitably stained with iron and haematoxylin, followed by safranine,* and, finally, mounted, after clearing with xylol, in Canada balsam. When less permanent mounts are required, glycerin jelly, mixed with a suitable stain such as methyl blue, may be used as a mounting medium; considerable expense and time are thereby saved.

The degree of softening desirable is ascertained by experience; but, given a really sharp knife and a good sledge microtome (Reichert's models and Jung knives give excellent results), a wood block should cut like rather hard cheese, at a thickness of 10 to 20μ.

It is usual to employ sample blocks of about 10 by 10 by 15 mm. in size, and to cut radial longitudinal, tangential longitudinal, and transverse sections, the last being the most useful for general diagnostic purposes.

Finally, in respect of the fourth class of material: it used, I believe, to be thought that charcoals were too hard and brittle to be sectioned in the usual way, but I found that a solution of commercial cellulose nitrate, known as "Celloidin," made as effective an embedding matrix for charcoals as it does for chitinous insects. The embedding is carried out in the usual way, on these lines: (1) Removal of all air from the tissues with a filter pump, while the samples are in 50 per cent. alcohol. (2) Desiccation, by means of graded alcohols, ending with a mixture of absolute alcohol and methyl ether (50:50). (3) Transference of the samples to air-tight screw-topped bottles, which are kept in an oven at 60° C., and contain celloidin dissolved in ether and alcohol; the concentration of the solution is increased, day by day, from 2 to 16 per cent. (4) Removal of the samples from the 16 per cent. celloidin, to be dropped into a mixture of ether and chloroform (50:50), in which they remain until hardened and ready to section.

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* A solution of a mixture of the alcohol-soluble and water-soluble safranines, in equal parts, is satisfactory. This, combined with haematoxylin, is excellent for photomicrography. Dilute solutions are best.

After sectioning, it is unwise to risk dissolving away the "Celloidin," which may be mounted, infiltrated as it is, with the section, either in glycerin jelly or in balsam. In this connection, I have found that good, clear mounts may be made by using Gurr's mounting medium, which appears slowly to dissolve away the celloidin, so clearing the section.

In microtoming, 95 per cent. alcohol may be used as lubricant, as in cutting ordinary wood blocks; nor have I found the use of the coloured commercial product to affect the results.

A much quicker and cheaper, though less perfect and reliable, technique than the latter is, first, to dry the charcoals, and then to dip them in a dilute solution of celloidin (or of cellulose acetate in acetone), re-painting the cut surface after each section. But, when used in this way, the solution tends to contract on drying, and it does not bind the tissues so thoroughly.

For soft, decayed wood samples, the cheaper and easier paraffin-wax method is suitable. But the technique is too well known for repetition here; xylol is used as paraffin solvent, with warming in an oven, during impregnation, as before.

In addition to these methods, impregnation with a synthetic resin was kindly tried for me, some while ago, at the Building Research Station (D.S.I.R.), where a resin of the following composition (in molecular weight proportions) has been found suitable for the preparation of thin sections of friable and weathered materials:—Phenol, 3; formaldehyde, 6; meta-cresol, 3 parts. In this way the very hardest materials can be successfully embedded and subsequently cut by a steel and diamond wheel, as in petrology; but, as the method is unnecessarily laborious and scarcely so successful as celloidin embedding, it need not be given in detail.

EXAMINATION AND IDENTIFICATION.—The chief diagnostic features, by means of which the wood of one genus may be distinguished from that of another, or—less commonly and surely—that of one species from another, are as follows:—

(i) The relative size, distribution, frequency and configuration of the *conducting vessels* (commonly known as "pores"), as seen in transverse section.

(ii) The relative size, distribution and frequency of the *medullary rays*, as seen in transverse and tangential longitudinal sections.

(iii) The type, grouping and distribution of the *wood fibres*,* as seen in transverse section.

(iv) The amount and arrangement of the vertical *storage parenchyma*, as seen in transverse and radial longitudinal sections.

(v) The presence, or absence, and disposition of vertical and horizontal *resin ducts*, as seen in transverse and tangential longitudinal sections.

These features are usually observable with a low-power microscope or hand-lens; but, in very closely similar woods—many of the conifers, for instance—it is

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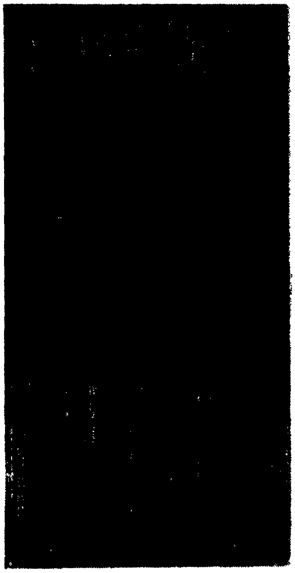
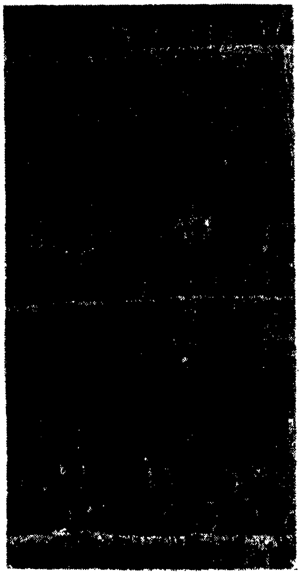
* The fibres are long elements, often occurring in bundles (*e.g.* in oak), which give mechanical strength to the wood. Fibres do not occur in conifers ("soft woods"), being replaced by thick-walled tracheids.

PLATE I.

STRUCTURE OF WOODS

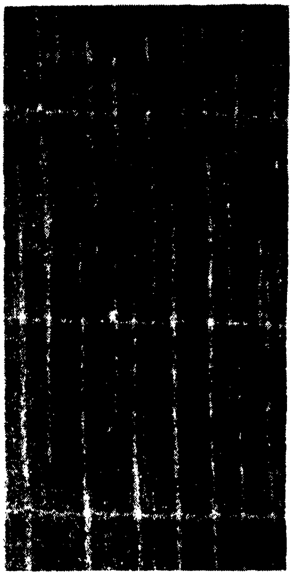


1
Scotch pine
(*Pinus sylvestris*)



2
Sweet chestnut
(*Castanea vesca*)

3
Common elm
(*Ulmus campestris*)



4
Field maple
(*Acer campestre*)

5
Hazel
(*Corylus avellana*)

6
Black poplar
(*Populus nigra*)

All are transverse sections, × 10 linear, as viewed under surface illumination.

often necessary to make use of yet more minute structures, such as are only visible in a good section and at high magnification; as, for example, pits in the cell walls, the height, width and frequency of the small rays, and the form of the cells composing the latter.

But, in not a few instances, two distinct species may resemble one another so closely that even these minute distinctions fail. Thus, from knowledge of the wood structure of a single small sample, it is often unsafe to deduce more than the broad *genus*. For instance, many species of elm are hard to differentiate, so are certain oaks; whilst the poplars and willows not only cannot safely be distinguished specifically, but poplar and willow woods may also be generically indistinguishable in surface view. And so on with other groups of closely related genera. The two related species, evergreen oak (*Q. ilex*) and white oak (*Q. alba*), however, would not readily be confused.

Reference to Plate I will illustrate the following diagnostic features:—Coniferous woods ("softwoods") are immediately distinguishable as a group from the Angiospermous flowering trees ("hardwoods") by the fact that they never possess vessels ("pores"), though they may, or may not, contain resin ducts—a group and generic distinction. (See Fig. 1.) Again, in a conifer, the more recently-formed wood of a growth-ring may, or may not, be sharply contrasted with the rest of the ring in the colour or thickness of its cell walls, or both. In conifers, the rays are always fine (Fig. 1); in the Angiosperms, they are sometimes fine and numerous (Figs. 2 and 6), sometimes thicker and less numerous (Figs. 3 and 4); and, occasionally, very large rays, visible to the naked eye, alternate with small ones (Fig. 5).

It will also be seen, from Plate I, that the "pores" in hardwoods are of variable size and arrangement, ranging from "diffuse porosity" (Fig. 4), by way of transitional forms (Figs. 6, 5 and 2), to marked "ring porosity" (Fig. 3)—*viz.*, a sharp transition, at the beginning of the ring, from large to small pores.

More detailed features need not be enumerated here. But one should add that, owing to the enormous number of woods of economic utility, it is a great help to the wood technologist in identifying unknown samples to be told, if possible, the country of origin. Yet, even that is of little avail when the region happens to be India, S. America, or Africa, for example, where the number of indigenous species runs into thousands, and whence others are still being imported. In all such cases, therefore, it is usual to construct both macroscopic and microscopic "keys," based upon the various anatomical characteristics mentioned above, *plus* features such as colour, hardness, taste, smell and density. These "keys," when comprehensively planned, facilitate the rapid identification of unknown wood samples. But individual variation and aberration from type are serious obstacles; a large collection of authentic wood samples and microscopic sections is, therefore, desirable in order that the wood technologist may also check his conclusions.

NOTES ON THE ILLUSTRATIONS.—*Plate I* represents surface views of small fragments of six common European woods, as seen in transverse section, magnified × 10 linear.

Plate II shows still smaller areas from transverse sections of three English woods (two being slow grown, with very narrow rings), as seen under the microscope by transmitted light, magnified × 30 lin. But, in this plate, only the upper three figures depict normal wood; the lower three are Roman charcoals of the same woods, submitted to me for identification, in which, similar, only slightly shrunken, tissues and elements may be recognised.

The charcoals were derived from a Roman smelting furnace, dating back to about 300 A.D., discovered in Surrey, and I am indebted to Mr. S. E. Winbolt for permission to use these photomicrographs, as well as to the Director of the Forest Products Research Laboratory, England, and Prof. C. C. Forsaith, of New York State College of Forestry, under whose direction the work here described was initiated.

3, RAWLINSON ROAD,
OXFORD.

DISCUSSION

Dr. CAMERON asked if there were any method for identifying charcoal when finely powdered.

Mr. MABY replied that this was very difficult, although occasionally in the case of an easily identifiable wood, such as common oak, he had been able to identify small splinters.

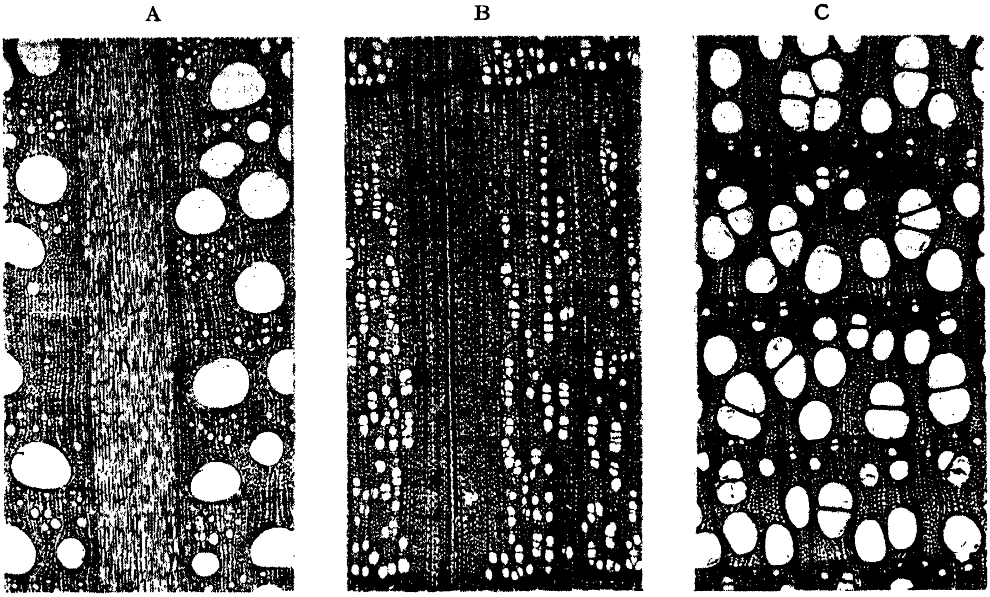
ADDENDUM.—Since the meeting my attention has been directed to a paper on "The Identification of Norit and other Wood Charcoals," by H. G. Tanner (*Ind. Eng. Chem.*, 1925, **17**, 191; ANALYST, 1926, **51**, 50). In an attempt to determine the nature of a highly activated decolorising charcoal called "Norit," which was introduced about 1911, it was found that minute particles of cell wall substance (apparently from the walls of conducting vessels or tracheids), termed "identification particles," were always present. These particles, examined under a high power of the microscope (say, ×500), were seen to be perforated by numerous minute pits, the relative size, frequency and pattern of which were seen to constitute a generic, if not also a specific, character. In this way it was concluded that "Norit" had been made from birch wood (*Betula occidentalis ?*).

I should add that I have not yet had occasion to employ the method myself, and a considerable amount of systematic work would be required before it could be put into practice; but, judging by what I have seen of cell-walled pitting in woods, it should prove satisfactory.

One possible objection which occurs to me is that the size, form and arrangement of such pits undoubtedly vary to a considerable extent within a given species, or even from part to part of a single cell wall. Moreover, a considerable amount of shrinkage (about 1/3?) takes place in wood when it is converted into charcoal. In incompletely charred specimens, therefore, the mean diameter of such pits might be greater than in specimens which have been treated for a longer period of time.

PLATE II.

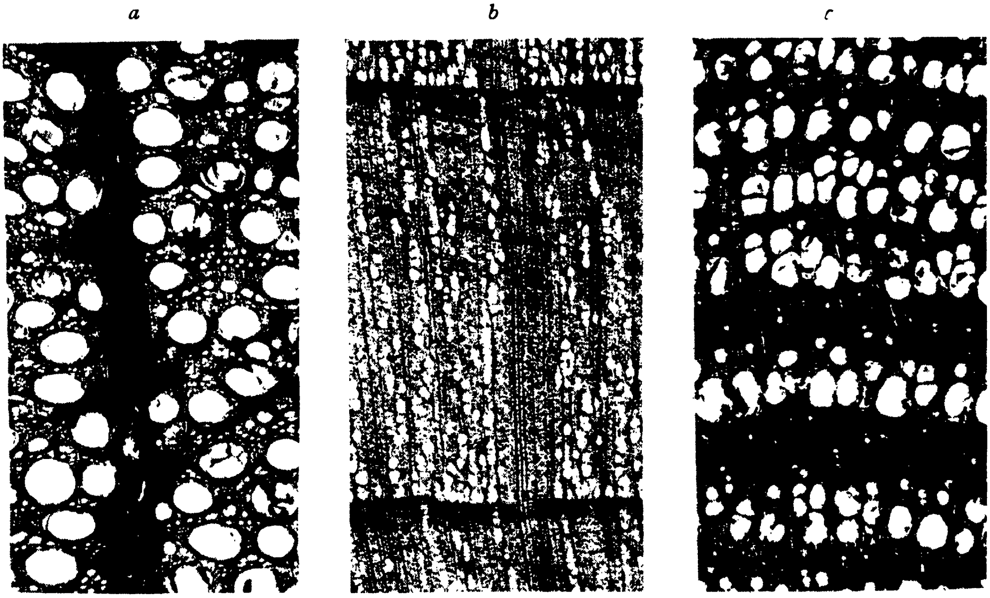
STRUCTURE OF WOODS



Common oak (*Quercus* sp.)

Hazel (*Corylus* sp.)

Ash (*Fraxinus* sp.)



Below: Roman charcoals (*a, b, c*) for comparison with the woods (A, B, C) shown above. All are transverse sections × 30 linear, as viewed by transmitted light.

The Extraction and Determination of Vanillin in Chocolate and Cocoa Butter

BY D. M. FREELAND, F.I.C.

(*Read at the Meeting, November 4th,* 1931)

THE flavour of vanilla is one that persists in popularity, especially in Britain. It is conveyed to chocolate and confectionery as vanillin, macerated vanilla pods, or as essences and extracts from the pods, which may be fortified with vanillin. Other natural materials containing vanillin, such as benzoin, may also be employed. The quantity of vanillin added seldom exceeds 0·1 per cent. of the finished article, as an excessive quantity results in an unpleasant after-flavour and affects the throat in an irritating manner.

Vanillin, resulting from the flavouring agent added to chocolate, is dissolved by the cocoa butter, and any method devised for its extraction must be able to cope with impurities inherent in a fatty solvent, especially those which lead to the production of emulsions. For the purpose of establishing a method of extraction, a 1 per cent. solution of vanillin in filtered, molten cocoa butter was prepared.

Vanillin is soluble in water to some extent. Durrans (*Perf. & Ess. Oil Rec.*, 1924, **15**, 239) quotes as its solubility 1·5 per cent. at 20° C., and 3·3 per cent. at 40° C. Shaking out the flavoured fat with warm water resulted in the recovery of a mere trace of vanillin. Winton and Silvermann (*J. Amer. Chem. Soc.*, 1902, **24**, 1128) have recommended the use of a 2 per cent. aqueous solution of ammonia for the removal of vanillin from de-alcoholised vanilla extracts.

Sufficient petroleum spirit (b.pt. 40°–60° C.) was added to 10 grms. of the flavoured cocoa butter to prevent solidification, and, after transference to a separating funnel, it was extracted with 2 per cent. aqueous ammonia. Emulsions formed, being assisted by the free fatty acids in the cocoa butter. These were difficult to disperse, but the addition of a little amyl alcohol materially assisted the separation.

Ammonia solutions of 2 per cent. (NH_3) concentration were prepared by adding the requisite quantity of ammonia solution (sp. gr. 0·880) to (*a*) methyl alcohol; (*b*) 50 per cent. (by vol.) aqueous alcohol; (*c*) 95 per cent. (by vol.) alcohol; and separate quantities of the flavoured fat were extracted by these solutions, respectively. The 95 per cent. alcohol and ammonia showed a sharp separation from the cocoa fat solution, and the tendency to form emulsions was small.

The following are details of the method finally adopted for the extraction: Twenty-five grms. of the melted fat are transferred to a cylindrical separating funnel of about 100 ml. capacity by means of petroleum spirit (b.pt. 40°–60° C.), using sufficient to prevent solidification of the fat when cool and to reduce its viscosity. An alcoholic ammonia solution containing about 2 per cent. of ammonia is prepared by diluting sufficient ammonia solution of 0·880 sp. gr. with 95 per cent. (by vol.) alcohol. The fat solution is shaken out with successive quantities of 10, 5, 5 and 5 ml. of the alcoholic ammonia, care being taken that as little fat as possible is removed when running off the alcoholic extracts into a glass evaporating basin of about 120 ml. capacity, in which they are united. If it is seen that globules of the alcohol remain dispersed to an extensive degree in the bulk of fat solution, the viscosity of that solution may be reduced by small additions of petroleum spirit, and this, combined with gentle agitation, will cause the globules to deposit. Forty ml. of water containing 18 ml. of *N* hydrochloric acid are added to the contents of the basin. Alcohol is then removed by evaporation upon a water-bath at 70° C. until the contents in the basin have been reduced to 20 ml. The liquid in the dish, with which are associated some oily globules (which experiment has shown cannot be neglected without loss of vanillin) is transferred to a separating funnel by means of warm water, followed by two or three washings with ether. When cool, more ether is added to the separator, which is then stoppered and shaken. The ethereal layer is separated, and three ethereal extracts of the aqueous portion are obtained. To the ethereal extracts, united in another separating funnel, are added 10 ml. of water, followed by 2 to 3 ml. of 2 per cent. aqueous ammonia (2 per cent. NH_3). After shaking out, the separated aqueous layer, together with any emulsion which accompanies it, is run into another separator, and the ether is extracted three times more, 5 ml. of water and 1 ml. of the dilute ammonia being used for each extraction. To the united and somewhat emulsified ammonia extracts is added saturated brine in sufficient quantity to "salt out" the emulsion. The almost clear aqueous layer is drawn off into a separating funnel, and followed by two small brine washings of the emulsion. The ammonia-brine extract is rendered just acid to methyl orange by addition of hydrochloric acid, and is extracted four times with ether, quantities of 15, 15, 10, 10 ml., respectively, being used. These ethereal extracts are put into a dry, tapped funnel, from which aqueous drainings are run off carefully. The ether is decanted into a weighed glass evaporating basin, followed by ethereal washings from the tapped funnel. The ether is allowed to evaporate spontaneously from the dish, floating on warm water, until about 3 ml. remain therein, and this is dissipated in a vacuum desiccator over sulphuric acid. When dry, the dish is allowed to gain equilibrium in the balance case, and the weight of crude vanillin is obtained.

The following results were obtained by the extraction of the prepared cocoa butter which was diluted with unflavoured butter, as detailed:

Flavoured cocoa butter. Grms.	Unflavoured cocoa butter. Grms.	Total fat extracted. Grms.	Vanillin content. Grm.	Crude vanillin recovered. Grm.
10	—	10	0·1	0·126
10	15	25	0·1	0·0998
5	20	25	0·05	0·0562
5	20	25	0·05	0·0596
5	20	25	0·05	0·0525
5	20	25	0·05	0·0493
5	20	25	0·05	0·0530

DETERMINATION OF PURITY.—The variation in the weights of crude vanillin from these different extractions proved that a method of determining the actual vanillin present was required. The risk of fatty acids being present with the vanillin in the crude extract prevented the use of a simple titration of the hydroxyl group, as suggested by Wellmann (*Pharm. Zeit.*, 1898, 634). Determination of the methoxy group by operations based on Zeisel's classic process called for special apparatus, as a micro-method was indicated. S. B. Phillips (ANALYST, 1923, 48, 368) reviewed methods depending on the aldehyde group, and described novel volumetric and gravimetric procedures, involving combination with that group. Many colorimetric methods have been recorded, but experience with some of these, when applied to vanilla essences, has revealed inherent failings in them.

H. J. Wichmann (*J. Assoc. Off. Agric. Chem.*, 1921, 4, 479) has suggested that sublimation affords a suitable means for the purification of vanillin. Quantities of 0·05 grm. of vanillin (prepared from eugenol) were subjected to sublimation in the apparatus devised by Monier-Williams for the purification of benzoic acid (ANALYST 1927, 52, 229). Conditions of temperature and duration of heating were varied, but not more than 0·034 grm. was recovered by this means. It was evident that part of the vanillin decomposes into guaiacol under sublimation conditions.

Attention was next focussed on Phillips's methods (*loc. cit.*), and attempts were made to adjust them to the small quantities of vanillin present in the crude extract. For the gravimetric process, Phillips takes 1 grm. of vanillin in a small beaker, adds 13·6 ml. of 0·5 *N* sodium hydroxide solution, and warms to assist solution. A solution of 2·4 grms. of semicarbazide hydrochloride and 5 grms. of crystalline sodium acetate in 30 ml. of water is filtered and stirred into the vanillin solution, and the mixture is heated in boiling water for ten minutes. After cooling, complete precipitation takes 4 hours, and the resulting precipitate is filtered off, washed free from chloride, and dried for 2 to 3 hours in a water-oven until constant in weight. The amount of semicarbazone, multiplied by 0·7271, gives the vanillin.

A tenth of the quantities of reagents given above were used when applying this procedure to crude vanillin residues obtained from 10 grm. quantities of flavoured cocoa butter. Upon adding the semicarbazide reagent to the warm vanillin solution, some precipitation was at once evident. The precipitate was inclined to be tacky, and in the first experiment was collected and filtered off with the semicarbazone, which separated upon cooling. In the second experiment only the flocculent and easily filterable semi-carbazone was collected. This procedure is open to criticism, and the adoption of the method was not further pursued, as the volumetric method, then in course of trial, was showing promise of giving speedier and better results. Typical results of the gravimetric experiments are indicated below:

Exp.	Extracting medium.	Crude vanillin recovered. Grm.	Vanillin from semi-carbazone. Grm.	Actual vanillin. Grm.	Recovery. Per Cent.
1.	Aqueous ammonia	0·180	0·1216	0·1	121·6
2.	Alcoholic ,,	0·126	0·0960	0·1	96·0

VOLUMETRIC METHOD.—One grm. of vanillin is dissolved in 20 ml. of 80 per cent. (sp. gr. 0·8484) neutral and pure alcohol. Inherent organic acidity is removed by the cautious addition of 0·1 *N* sodium hydroxide solution, with methyl red as indicator, and 1·1 to 1·2 grm. of pure *p*-toluidine is dissolved in the liquid. Twenty ml. of 0·5 *N* sodium hydroxide solution are added, and 100 ml. of cold water (free from carbon dioxide) are poured in. The liquid is then titrated rapidly (to avoid absorption of carbon dioxide) with 0·5 *N* sulphuric acid until a permanent turbidity is noted. The difference between the volumes of 0·5 *N* alkali and acid, multiplied by 0·076, gives the amount of vanillin present.

Upon trying this method, using small quantities of vanillin, the conditions outlined above had to be altered materially in order to obtain the turbid end-point. The influence of the quantity of alcohol present was most marked, and, if in slight excess, the production of the end-point was entirely nullified, although the depth of tint indicative of it was maintained; the addition of excess of water, or a similar effect obtained by the use of too great a volume of standard alkali, also destroyed the end-point turbidity.

The conditions adopted for a satisfactory end-point, as applied to weighed quantities of vanillin, are as follows:—The vanillin, weighed upon a watch-glass, is transferred to a clear glass specimen tube, 4" × ⅞", by means of the necessary quantity of 80 per cent. alcohol, as shown below. A drop of methyl red indicator is added, followed by sufficient 0·02 *N* sodium hydroxide solution to effect the neutral colour change. Then, pure *p*-toluidine, weighed within 0·01 grm. in excess of the vanillin taken, is added to the tube, dissolved by shaking, and 5 ml. of 0·1 *N* sodium hydroxide solution are added from a burette, followed by the amount of water indicated below. The liquid is back-titrated to the turbid end-point with 0·05 *N* sulphuric acid, added from a burette graduated in 1/20th ml. (1 ml. of 0·05 *N* alkali = 0·0076 grm. of vanillin).

Vanillin. Grm.	Alcohol (80 per cent.). Ml.	Water. Ml.
0·04	0·8	–
0·05	1·0	1
0·06	1·2	2
0·07	1·4	2

The following results were obtained:

Vanillin taken. Grm.	0·1 *N* NaOH taken Ml.	Back-titration 0·05 *N* H_2SO_4 Ml.	Combined 0·05 *N* NaOH, from mean back-titration. Ml.	Vanillin found. Grm.
0·04	5	4·65 4·63	5·36	0·0407
0·05	5	3·36 3·46	6·59	0·0501
0·06	5	2·06 2·07	7·93	0·0603
0·07	5	0·71 0·68	9·30	0·0707

Certain slight modifications are necessary when applying the method to the determination of the vanillin present in the crude extract. If the residue is taken up in 80 per cent. alcohol, impurities dissolve with the vanillin and produce a turbidity in the solution before the final titration can be applied. Impurities are eliminated in the following manner:

The crude residue in the glass basin is extracted with 2 ml. of alcohol (40 per cent. by vol.). It is advisable to warm the basin slightly; the residue is thus loosened from the side, and part appears as oily globules on the surface of the alcohol. After cooling to about 15° C., the liquid is decanted through a disc of filter paper in a small Hirsch funnel, which, with an accompanying tube for attachment to a water-pump, passes through a double-bored stopper fitting the specimen tube. The residue in the basin is extracted thrice more in like manner, using 1 ml. of 40 per cent. alcohol each time, and pumping each washing dry from the funnel before adding its successor. Alcohol is then evaporated from the contents of the tube. This is done expeditiously by aspirating air through the tube, which is placed in a water-bath at about 50° C., until a volume of about 2 ml. remains. Free acidity is neutralised, and a suitable quantity of *p*-toluidine is added. This quantity approximates the weight of the crude extract, and if this is under 0·04 grm., the *p*-toluidine should not exceed its weight. Strong alcohol is added, drop by drop, until, on shaking, solution takes place. At this point the anhydro complex may be thrown out as a canary-yellow precipitate. From this point the procedure for final titration, as detailed above, is followed.

Typical results obtained are tabulated below:

Actual vanillin in cocoa butter. Grm.	Crude vanillin extracted. Grm.	Vanillin found by titration. Grm.		Recovery. Per Cent.
0·05	0·0793	0·0421		84·2
0·05	0·0530	0·0426		85·2
0·05	0·0562	0·0436		87·2
0·05	0·0596	0·0479		95·8
0·05	0·0525	0·0456		91·2
0·05	0·0493	0·0424		84·8
			Mean	88·0

With regard to the first result above (showing 84·2 per cent. recovery), the vanillin was first extracted from the crude material by sodium bisulphite. The bisulphite compound was decomposed, and the vanillin recovered weighed 0·042 grm. This, when dissolved and titrated, gave 0·0421 grm. of vanillin.

It may be concluded, therefore, that the extraction process previously described results in the recovery of 88 per cent. of the 0·2 per cent. of vanillin contained in cocoa butter.

VANILLIN FROM CHOCOLATE.—The fat from chocolate is first extracted. Most of it can be removed simply by placing the broken-up chocolate in a flask, covering it with petroleum spirit (b.pt. 40° to 60° C.), warming gently, and shaking the contents until the solid lumps have disintegrated. The chocolate suspension is transferred to a tall glass cylinder, and the solids are left to settle overnight. By applying slight suction to a flask, the clear fat solution can be drawn over by means of a tube, bent up at the end, and inserted carefully to such a depth in the cylinder that the solids remain undisturbed. Further shakings with solvent, settling and withdrawal of the supernatant liquid can be given, if desired, until the chocolate is exhausted. The fat solution is filtered, and the solvent is recovered at a low temperature. The last traces of solvent are removed from the fat by applying heat which is insufficient to cause loss of vanillin by volatilisation.

The amounts of vanillin in the cocoa butter thus obtained from two chocolates were determined.

Chocolate A.—Cocoa butter content = 31·09 per cent.

Extraction No.	Cocoa butter extracted. Grms.	Crude vanillin obtained. Grm.	Vanillin content of crude extract by titration (in 25 grms. butter). Grm.
1.	25	0·0420	0·0289
2.	25	0·0410	0·0306
3.	25	0·0660	0·0303
		Mean	0·0299

Vanillin content of chocolate according to mean recovery = 0·0372 per cent.

Chocolate B.—Cocoa butter content = 32·33 per cent.

1.	30	0·0085	0·0068
2.	25	0·0072	0·0055
3.	25	0·0060	0·0049
4.	25	0·0216	0·0057
		Mean	0·0057

Vanillin content of chocolate according to mean recovery = 0·0075 per cent.

The high crude vanillin weights obtained in extractions A3 and B4 are explained by the use of stronger aqueous ammonia, which resulted in more impurity being carried forward in the subsequent extraction stages. The low weight of crude vanillin obtained by the extraction of the cocoa butter from Chocolate B necessitated adjustment of the quantities of reagents used for the titration process. Thus, 1 ml. of 0·1 *N* sodium hydroxide solution was employed, instead of 5 ml., as indicated in the procedure.

The results obtained from the chocolates can be adjusted by taking into account the figure of 88 per cent., the mean recovery of vanillin from cocoa butter containing 0·2 per cent.

The method described for the extraction should serve equally well for fatty materials other than cocoa butter which contain dissolved vanillin.

I wish to thank the Directors of Messrs. Macfarlane, Lang & Co., Ltd., for permission to publish these results.

THE LABORATORY,
MESSRS. MACFARLANE, LANG & CO., LTD.,
FULHAM, S.W.6.

DISCUSSION

Mr. C. E. **SAGE** asked if there were any means of detecting vanillin made from the vanilla bean, as apart from the three synthetic kinds of vanillin. He, personally, had to rely on his sense of smell to distinguish between the four kinds of vanillin in use, but he would like to know if this could be done chemically.

Mr. G. N. **GRINLING** asked whether the method would be of any use for the cream fillings used in biscuits, Swiss rolls, etc. Also, had it been applied to vegetable oils, as apart from cocoa butter, or to substances on the market claimed to be four times as strong as vanillin? Had the author considered centrifuging as a means of accelerating the separation? He had frequently centrifuged fats in cocoas, and got good results very much more quickly than in the manner described.

Mr. **FREELAND**, replying to Mr. Sage, said that he was unaware of any chemical means of distinguishing vanillin derived from the vanilla bean from that manufactured synthetically. He suggested, however, that little vanillin was extracted from the vanilla bean for use as such, as anyone desiring to use the natural principle would surely employ the bean.

Replying to other questions, he said that, provided moisture was eliminated from cream fillings, it was possible to follow the process indicated for cocoa butter. Many of the vanillin substitutes on the market consisted of ethyl-vanillin. He had not tried his method on this substance. He acknowledged that centrifuging would be helpful, but he had not been able to do this on account of the volume of liquid being too great.

Food Control in Holland

BY A. VAN RAALTE, D.SC., AND J. STRAUB, CHEM.ING.

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(Abridged from the Paper read at the Meeting, February 4th, 1931)

PRIOR to the Dutch Pure Food Act of September 19th, 1919, the legal basis for the fight against the adulteration of food rested on municipal decrees in several towns, and lacked sufficient juridical support.

The principal paragraphs of the new Act forbid and impose severe penalties for the sale of foodstuffs which may be injurious to health, or are of incorrect composition or are unsound. Foodstuffs are considered to be of incorrect composition, not only when they are adulterated, but also when they are naturally defective, as, for example, if the proportions of their effective constituents are below the accepted standard for the trade. The definition given in that Act, of the term "incorrect composition," was made very elastic, so that the Directors of the Food Inspection Services might use different standards so long as no Order in Council had established legal standards for all the various articles, as by now has practically been done. The initial difficulties have been surmounted by agreements between the directors of Food Services and reputable large manufacturers, and some of these local trade standards have subsequently served as the basis for Orders in Council.

It should be mentioned that the Dutch Act, although described as the Pure Food Act, was in reality projected with a wider scope. Any article of commerce can, by Order in Council, be brought within the range of this law, and then has to comply with the conditions laid down in the principal paragraph of the Act, *viz.* that it must be of correct composition and in sound condition, and not liable to cause injury to health when used for its normal purpose. Up to the present the following articles, other than foods, have been brought, by Orders in Council, within the scope of the Act:—(1) All articles intended to be used or used in the preparation of food or drink; (2) all articles intended to be used or used for the packing of food or drink; (3) wallpaper and curtains; (4) toys; (5) rubber articles used in connection with the feeding of infants; (6) toilet articles and cosmetics; (7) spoons, forks and other household implements; (8) articles for washing and bleaching, and for polishing and dyeing of leather; (9) substances for destroying insects and other noxious animals; (10) kapok.

For some of the articles in this list special limits and standards have been fixed, such as, for example, for the arsenic content of wallpapers and tapestries, and for the composition of soap, washing and bleaching powders, and kapok. In addition, there is an Order in Council, the so-called General Decree, on the hygienic conditions of shops where food is sold, and very severe regulations have been made for the milk trade, so as to ensure progressive improvement in the hygienic production, transport and distribution of milk.

The Act makes it obligatory on municipalities to organise the inspection of foods, and authorises penalties not exceeding a fine of 2,000 fl. or 6 months' imprisonment. All municipalities have the same regulations controlling the sale and distribution of food, etc., or of articles which, although used for their proper purpose, might be injurious to life or health. The basis of the control is thus both national and municipal; it ensures national unity in standards, but leaves to the local authorities the power of accommodation to local conditions.

The Control is carried out by twenty-one Food Inspection Services, each of which controls the trade in its central municipality by means of a technical inspection staff and a chemical staff. Before any prosecution is instituted independent analyses are made by two chemists. The vendor is entitled to require the inspector to seal a second sample to be left with him. Inspectors have the power of entering at any time premises where food is prepared or kept, but, if the occupier of the premises also lives there, the inspectors can enter only after producing a written permit signed by a judge or mayor.

The Orders in Council are based on drafts drawn up by a Commission which acts in co-operation with representative manufacturers and tradesmen, and these drafts are first submitted to the trade organisations.

The Act authorises a manufacturer or a group of manufacturers to prepare their products under the supervision of a private institute, and to publish an announcement to this effect. So far, no one has taken advantage of this permission.

The appointment of the Director of a Food Service has to be confirmed by the Government. The inspection services, however, are administered by the respective central municipalities. The Government pays half of the yearly expense, and the other half is paid by the municipalities belonging to the district of the inspection department, according to the number of their inhabitants.

The smallest service is that in Leyden, with a population of 208,000; the largest that in Amsterdam, with a population of 835,000. In 1929 the Food Inspection Department in Amsterdam inspected 548,090 lots of foodstuffs, and 41,849 samples, of which 28,204 were milks, were examined in the laboratory.

INSPECTION OF MILK.—Although the inspectors have power to make a preliminary examination of all articles, in practice this is done only with milk. The inspectors test milks with the lactometer, and also apply Storch's reagent (in the form of powder) to ascertain whether the milk or cream is pasteurised (73° C.), but there is a rule that the inspectors have to bring in samples not only of suspected milk, but also of milk that seems to them from the lactometer reading to be genuine. Among these unsuspected samples there may be some which have been brought to the correct specific gravity by the addition of both water and skim milk. As a matter of fact, several skilful adulterators have confessed that they worked in this way for many years without ever coming into conflict with the Inspection Department. Most of them were found out by the cryoscopic method, which is in daily use in every laboratory for milk analysis in Holland. It is not necessary, of course, to "freeze" every one of the hundred, or so, samples brought in each day, but it seems reasonable to suspect of being watered every milk which gives a result for solids-not-fat 0·20 below the mean result for genuine milk samples of the same day. Indeed, by statistical examination of the results given by milk from farmers it would be possible to prove that milk diverging by more than 0·2 per cent. in solids-not-fat, or by 0·3 per cent. in fat, may be suspected of adulteration. If all the analyses of farmers' milk over a period of a few days are plotted as a graph, an ellipse can be drawn in such a way that half of the samples are inside, and the other half evenly distributed in different directions outside the ellipse. It is reasonable to regard the latter as abnormal, and, in so far as their analytical results are low, as suspicious or incorrect. We have drawn such ellipses for each of the months of different years, and have found that, although, of course, their centre changes with the mean composition of the milk in different seasons, their dimensions are fairly constant, so that the critical number of 0·2 for solids-not-fat and 0·3 for fat may be used throughout the year for Dutch farmers' milk, sampled from the original 50-litre cans.

When the Food Inspection Service in Amsterdam, in its present form, first came into operation (in 1921) the statistics showed that about 40 per cent. of the milk samples taken were adulterated. From that time onwards 30,000 samples a year were analysed in the laboratory, with the result that in 1930 only 3 per cent. of the samples were condemned as adulterated.

In 1924 the hygienic examination of milk was begun. The milk is first examined for visible dirt, and the numbers of streptococci and bacteria are determined (standard: less than 1,000,000 bacteria per c.c., or, what comes to about the same thing, a reductase time of less than 3½ hours, as determined by a slightly modified form of Barthel's method).

More recently some 300 samples per annum have also been tested for tuberculosis bacilli, and the number is to be increased in future. Improvement has already resulted from these examinations. The percentage of samples containing streptococci decreased from 13 per cent. in 1926 to 7·5 per cent. in 1929. About 70 per cent. of the samples of raw milk were bacteriologically sound (low reductase number). For the last four years stalls and utensils have been systematically controlled by a special stall inspector, and it is now estimated that 70 per cent. of the stalls and of the cattle reasonably satisfy the requirements. Further improvement is somewhat handicapped by the difficult economic position of dairy farmers.

Milk from farms within 20 miles of Amsterdam is best delivered raw in the original cans sealed with a lead seal bearing the farmer's initial. Milk coming from other districts must be pasteurised, unless a special permit has been obtained for it to be imported in the raw condition. Pasteurised milk (Storch test,* negative, 25,000 bacteria per c.c.) and pasteurising plants are also supervised. About 16 per cent. of the milk is supplied in the pasteurised state.

GENERAL INSPECTION WORK.—The inspectors visit each grocery shop at least once a quarter, and dairies and bakeries once or twice a month. A prosecution is only instituted when it is clear that a simple warning is ineffective. By means of such written and verbal warning *bona-fide* traders have gradually been taught how to comply with the rules for composition and labelling promulgated from time to time for special categories of foodstuffs.

INSPECTION OF BREAD.—Two inspectors (bread experts) visit the bakeries, from day to day, and weigh the loaves. As a rule, they can draw conclusions by examining the exterior of the loaf (*i.e.* whether thoroughly baked or not). If they are in doubt whether it answers to the statutory requirement as to dry substance, they bring a loaf to the laboratory for the determination of moisture. Thanks to these intensive inspections, the delivery of short-weight loaves is becoming more and more rare.

EFFECT OF THE ORDERS IN COUNCIL.—In every category of food the percentage of unsatisfactory samples showed a sudden increase after the respective Orders came into force, followed by a gradual decrease as the more severe requirements were complied with, except in certain cases where the figures did not take the expected course, owing to special causes. For example, the figures for jam would have shown the usual course, but for the detection, in 1929, of the use of formic acid as a preservative. This is prohibited, and 23 samples were condemned, with the result that there was a sudden increase in the percentage of adulterated samples for that year. The figures for meat are also unsatisfactory, owing to the difficulty of curing butchers of the habit of using flour and artificial colour in sausages, although the results appear more unsatisfactory than they really are, because the inspectors visit the premises of offenders more frequently than before and bring in all sausages in which they can detect any signs of adulteration.

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* The Storch test is the Continental name for Dupouy's paraphenylenediamine test; *cf.* A. E. Leach, *Food Inspection and Analysis* (John Wiley & Sons, New York, 1920), p. 173.

Summary of the Principal Regulations under the Dutch Food Law

The same principle is adopted for all regulations. The name, in Dutch, under which an article is sold must be on the package, or on a shield directly above, if the article is sold loose (except in the case of certain articles sold wholesale, and for some where no misunderstanding can take place, such as sausages or bread).

The names allowed are tabulated in the regulations, and, as a rule, with a definition of the article, and with a statement of the chemical requirements, apart from the general rule that every article must conform in its properties with those described, that it must not have deteriorated, and must not contain foreign matter other than, or in greater quantity than, is expressly allowed by the regulation in question.

For goods of better quality, some subsidiary names are allowed, the use of which is protected but not obligatory. For control, the methods of analysis given in appendices to the different regulations must be used, in so far as these are sufficient for the detection of adulteration. To prevent circumvention, every regulation contains a paragraph to the effect that goods bearing a likeness to, or likely to be sold as a substitute for, those mentioned in the respective regulations are not allowed in the trade under names that do not distinctly show their character and composition. The principal articles for which standards have been fixed are summarised below in order of date. The obligatory Dutch denominations have been translated into English.

BREAD. (May 24th, 1922.)

Strict hygienic local control. The weight of a loaf is based on a minimum weight of solids (240 grms.).

White Bread.—*Solids*, 240 grms., or a multiple thereof, per loaf; *salt*, less than 2·5 per cent.; *ash other than salt*, less than 1 per cent

Brown Bread.—*Solids*, 225 grms., or a multiple thereof, per loaf; *ash other than salt*, less than 2·4 per cent.

Rye Bread.—*Solids*, 260 grms., or a multiple thereof, per loaf; *ash other than salt*, less than 2·4 per cent.

White Milk-bread.—*Solids*, 240 grms., or a multiple thereof, per loaf; *ash other than salt*, less than 1·5 per cent.; *fat*, over 3 per cent.; *milk-fat*, over 1·6 per cent. on the solids (Kirschner value product of fat = 30; *i.e.* the product of the Kirschner value of the fat and the percentage of fat on the solids; *cf.* Leach, p. 551).

Cream-bread.—*Fat*, over 4·5 per cent.; *Reichert–Meissl value*, over 15; *Polenske value*, less than 2·2.

SUGARS AND SYRUPS. (June 6th, 1924.)

Candy (white), yellow candy, sugar (white), yellow sugar, milk-sugar, starch-sugar, starch-syrup (all with a fair allowance for ash and non-sugar, SO_2 40 mgrms. per kilo.).

Candy Syrup.—*Solids*, 80 per cent.; *ash*, 1·5 per cent.; *non-sugar*, less than 16 per cent.

Sugar Syrup.—*Solids*, 80 per cent.; *ash*, 5·0 per cent.; *non-sugar*, less than 21·6 per cent.

Household Syrup.—*Solids*, 80 per cent.; *ash*, 5·0 per cent.; about 50 per cent. *starch syrup*.

Kitchen Syrup.—*Solids*, 80 per cent.; *ash*, 4·0 per cent.; about 75 per cent. *starch syrup*.

Melado, Molasses.—No regulations as to composition, but must conform to the general regulations.

SPICES. (August 19th, 1924.)

No addition of any foreign matter is allowed (salt, colour or preservative). Chemical standards are fixed for all kinds of spices; they are well below those given by samples of the respective spices of the ordinary trade qualities.

Mustard.—*Water*, 75 per cent.; *salt* (on solids), 15 per cent.; *salt-free ash*, 8 per cent. (on solids); *sand*, 1 per cent. (on solids); *sulphate* (SO_4), 1·5 per cent. on mustard.

PRESERVED MEATS. (August 20th, 1924.)

Feder number,* 4·0 per cent.; saltpetre, 0·2 per cent. (no colouring matter).

Minced Meat, Raw Sausages, Canned Meat, Boiled Sausages.—*Starch*, 4 per cent.

Liver Sausage.—*Starch*, 4 per cent.; *boric acid*, 0·3 per cent.

MARMALADES, FRUIT JUICES, LEMONADES. (September 6th, 1924.)

Jam.—*Water*, 35 per cent.; from fruit and sugar only; small allowance for addition of other fruit than mentioned on label. There is no minimum requirement for total fruit content; but at least 75 per cent. must be of the sort indicated on the label. For pine-apple jam, cherry jam, and morella cherry jam, however, the minimum requirement is only 60 per cent.

(* The Feder number is the ratio of water to organic fat-free solids; *cf.* Leach, p. 222.)

Household Jam.—*Water*, 35 per cent.; from fruit, sugar and starch syrup, artificial colour, 250 mgrms. of benzoic or salicylic acid per kilo. (large allowance for addition of other fruit).

Fruit Jelly.—*Water*, 35 per cent.; from fruit juice (30 per cent.) and sugar only (small allowance for addition of other fruit juice).

Fruit Juices.—Addition of 400 mgrms. of salicylic acid or benzoic acid per kilo. and 50 mgrms. of total sulphur dioxide per kilo.

Fruit Syrup.—*Genuine juice*, 30 per cent.; *sugar*, 55 per cent.

Acidulated Fruit ("Limonade") Syrup.—*Genuine juice*, 30 per cent.; *sugar*, 55 per cent.; *essential oil, vegetable colour, citric acid*; 20 mgrms. of *sulphur dioxide* per kilo; 250 mgrms. of *salicylic* or *benzoic acid.* **Pine-apple Syrup** must contain 15 per cent. of pine-apple juice.

Acidulated Syrup.—*Sugar*, 55 per cent.; *essential oil, colouring matter, citric acid or lactic acid.*

Effervescent Lemonade.—Lemonade syrup with water and carbonic acid, *sugar*, 8 per cent.: foam stabiliser allowed, but no saponin.

TAPESTRY. (October 29th, 1924.)

Arsenic, not to exceed 100 mgrms. per sq. metre.

WALLPAPER.

Arsenic, not to exceed 5 mgrms. per sq. metre.

MEAT EXTRACTS. (November 23rd, 1924.)

Salt and spice are the only additions allowed.

(Solid) Extract of Beef.—*Water*, 20 per cent.; *creatinine*, 6 per cent. of solids.

Liquid Extract of Beef.—*Water*, 68 per cent.; *creatinine*, 1·5 per cent. of solids.

Beef-tea.—*Water*, 85 per cent.; *creatinine*, 1·5 per cent. of solids.

Cubes.—*Salt*, 65 per cent.; *creatinine*, 0·5 per cent. of solids.

FLOUR AND STARCH PRODUCTS. (December 20th, 1924.)

Artificial colour, bleaching agents, baking powders (no alum) allowed. Chemical standards well below numbers for current trade qualities. The following come within the regulation: All kinds of flour, flakes, starch, malted meal, dextrinised and treated flour, custards, pudding jellies, macaroni, etc. The preface "egg" is allowed for products containing 55 grms. of egg yolk or 150 grms. of whole eggs per kilo.

COFFEE, TEA AND THEIR SUBSTITUTES. (February 3rd, 1925.)

The lowest standards occurring normally in trade qualities.

Caffeine-free Coffee.—*Caffeine*, 0·1 per cent.

Coffee-extract.—*Solids* (non-sugar), 6 per cent.; *caffeine*, 2·5 per cent. on solids (non-sugar).

PAPER. (April 1st, 1925.)

A quire has been fixed at 25 sheets, a ream at 20 quires. Standards for quality have been fixed, giving a right to the use of special watermarks, numbers and letters.

HONEY AND HONEY SUBSTITUTES. (August 28th, 1925.)

Honey.—*Solids* (natural), 75 per cent.; *sucrose content*, less than 5 per cent.; absence of oxymethylfurfural; *acidity*, 5 c.c. of *N* acid per 100 grms.; presence of diastatic enzymes.

Heated Honey.—The same, except for absence of diastatic enzymes.

Artificial Honey.—*Solids*, 75 per cent.; *ash*, 0·5 per cent.

MILK AND PRODUCTS FROM MILK. (October 7th, 1925.)

System of licensed retailers; high hygienic requirements locally.

Milk.—*Freezing-point*, −0·53°; sp. gr. of *serum*, 1·0240 at 15·0°/15·0° C.; *refraction*, 1·3420 at 17·5° C.; *acidity*, 9·0; no dirt; no streptococci.

Pasteurised Milk.—The same; no *B. coli*; *bacteria*, not more than 25,000 per c.c.

Separated Milk.—The same, except for *fat*, less than 1 per cent.

Cream.—*Fat*, over 20 per cent.

Whipped Cream.—*Fat*, over 40 per cent.

Butter-milk.—*Solids-not-fat*, above 7·3 per cent.; *milk sugar*, above 3 per cent.; *acidity*, equivalent to 20 to 40 c.c. of 0·25 *N* alkali per 100 c.c.

COCOA AND CHOCOLATES. (January 1st, 1926.)

Cocoa Powder.—*Fat*, over 22 per cent. (on solids); *shell*, less than 4 per cent. on solids-not-fat; *water*, less than 9 per cent.; *ash*, less than 14 per cent. (on solids-not-fat).

Second-grade Cocoa Powder.—*Fat*, 15 to 22 per cent.

Chocolate.—*Cocoa, sugar*, necessary additions for flavour and taste; *cocoa content*, 32 per cent.

Milk Chocolate.—*Cocoa content*, 25 per cent.; *milk solids*, 12·5 per cent.

MARGARINE. (February 1st, 1926.)

Margarine.—*Salt, ad lib.*; *water*, less than 16 per cent.; *fat*, over 80 per cent.; *benzoic acid*, less than 0·2 per cent.

Margarine Mixture.—The same, with 15 per cent. of genuine butter (Kirschner value, 3·0).

DETERGENTS. (February 5th, 1926.)

Soft soap fatty acids, 38 per cent.; hard soap I, 60 per cent.; hard soap II, 40 per cent.; hard soap III, below 40 per cent.; soap-flakes, 80 per cent. of fatty acids; all these with small allowance for alkali carbonate and hydroxide.

Soda Crystals.—36 per cent. of *Soda ash*, and 95 per cent. of Na_2CO_3.

Bleaching Powder.—*Active chlorine*, 25 per cent.

Soap-powder I.—*Fatty acids*, 35 per cent.

Soap-powder II.—*Fatty acids*, 30 per cent.

Washing Powder.—*Fatty acids*: 10 to 25 per cent.; declaration of percentage of fatty acids on package obligatory. *Oxidising Agent and Water-glass* allowed with declaration.

BEER. (November 1st, 1926.)

Original wort, 9 per cent. *Ratio of extract to alcohol*, 0·8–2·5; *saccharin*, 1·5 grm. per *hl.*; *caramel; sulphur dioxide*: 25 mgrms. per litre.

VINEGAR. (January 1st, 1927.)

Vinegar.—*Acetic acid*, 4 per cent.; additions of salt and caramel allowed.

Double Vinegar.—*Acetic acid*, 8 per cent.

Vinegar with Indication of Origin (*e.g.* beer-vinegar, malt-vinegar, raisin-vinegar).—*Acetic acid*, 4 per cent. by fermentation only; *solids other than salts*, more than 0·7 per cent.

Wine Vinegar.—The same, except for *acetic acid*, 5·5 per cent.

Spirit Vinegar.—The same, except for *acetic acid*, 8·0 per cent.

Solution of Acetic Acid.—*Acetic acid*, 12·5 to 80 per cent.

Acetic Acid Essence.—*Acetic acid*, 80 per cent.

OILS AND FATS. (April 1st, 1927.)

These must be free from water; *acidity*, equivalent to less than 8 c.c. of *N* alkali per 100 grms. When sold without indication of origin, artificial colour is allowed; with indication of origin (*e.g.* beef-fat, olive oil), no colouring allowed. The use of inedible fat in factories is subject to special supervision.

CHEESE. (July 1st, 1928.)

Every cheese must bear a mark indicating its fat content (on solids):

Lean, "**Mager.**"	—Below 20 per cent.
20+	Between 20 per cent. and 30 per cent.
30+	Between 30 per cent. and 40 per cent.
40+	Between 40 per cent. and 48 per cent.

V.V. or Volvet.—Over 48 per cent.

R.65.—Over 65 per cent. (cheese made from cream).

ICE CREAM. (August 16th, 1929.)

Milk Ice.—There is a system of licensed producers and retailers. Strict hygienic control. Storch reaction negative; bacterial count, 100,000; *B. coli*, negative; artificial colour allowed.

Ice Cream.—The same, with 12 per cent. of *milk-fat*.

WINE AND CIDER. (January 1st, 1930.)

Wine.—Every wine must have the composition, colour, odour and taste, characteristic of the sort for which it is offered (Art. 7). When an origin is expressly mentioned, the wine must conform to the standards prevailing in trade for this sort of wine of the mentioned origin (Art. 8). *Potassium sulphate,* 2 grms. per litre; *sulphur dioxide* (total), 450 mgrms., (free) 45 mgrms. per litre.

Fruit Wine (Cider).—*Fruit juice,* 30 per cent.; *benzoic acid,* 300 mgrms. per litre; or *sulphur dioxide* (total), 200 mgrms., (free) 20 mgrms. per litre; *caramel, amaranth,* and *ponceau* permitted.

KAPOK. (July 1st, 1930.)

Java kapok must be genuine and labelled. Kapok mixtures with other fibres must be labelled and percentages given correctly.

EGGS. (September 1st, 1931.)

Definitions of different qualities of eggs are given in accordance with recognised trade standards.

Eggs of all sorts must be marked to indicate the quality, with the exception of genuine fresh eggs, on which a mark to this effect is permissible, but not obligatory.

Fresh Eggs.—Eggs which have not been submitted to any means of preservation. No marking necessary.

"Foreign fresh eggs" must be sold under this designation.

Cold-Storage Eggs.—Eggs which have been kept at any time in cold storage.

Preserved Eggs.—Eggs which have been treated with lime, silicate, or the like.

Second-Grade Eggs.—All other hens' eggs fit for consumption.

Keuringsdienst van Waren,
Keizersgracht, 732–734, Amsterdam.

The Analysis of Cadmium Red Pigments

By CHARLES GASPARD DAUBNEY, M.Sc., A.I.C.

Cadmium red is usually a mixture of cadmium selenide, cadmium sulphide and barium sulphate. In spite of its comparatively simple composition, considerable difficulty has been experienced in the analysis of samples of this material. An investigation of the methods of analysis available was consequently undertaken.

Previous to the work to be described, the method employed was as follows:

(1) Extraction of the material with nitric acid, until free from colour, diluting with water, and filtering off the insoluble barium sulphate.

(2) Adding hydrochloric acid and potassium chloride to the filtrate, boiling, and precipitating the selenium with sulphur dioxide.

(3) Passing hydrogen sulphide into the filtrate to precipitate cadmium sulphide, and converting the sulphide into sulphate.

When this procedure was used it was found (*a*) that the results for selenium were variable; (*b*) that the analytical figures always added up to less than 100 per cent.

The discrepancies indicated the unsatisfactory nature of the method of determining selenium, and suggested that the extraction of the original pigment might be incomplete. Further, it was felt that the process of determining cadmium, although the accepted method, left something to be desired.

As a standard for testing the accuracy of the various processes involved, the possibility of compounding a cadmium red of known composition was considered. As it was difficult to obtain pure cadmium selenide, pure cadmium selenate was prepared and employed as a standard source of cadmium and selenium.

PREPARATION OF CADMIUM SELENATE.—Ten grms. of cadmium carbonate were suspended in water and 13 ml. of selenic acid (Δ 1·4) were added. The mixture was warmed on a steam-bath, and, after action had ceased, the solution was filtered and concentrated in a silica dish. After cooling, the mother liquor was poured off, the crystallised cadmium selenate was dissolved in water, re-concentrated (but not sufficiently to cause crystallisation), and the aqueous solution was treated with absolute alcohol. The cadmium selenate was thrown down as a fine white powder, which was filtered off by suction, dried gently to remove alcohol, ground finely and finally dried at 105° C. until constant in weight. Van Hauer (*J. prakt. Chem.*, 1860, [1], **80**, 214) states that by drying at such a temperature $CdSeO_4,H_2O$ results. In addition to confirming the percentage of cadmium and selenium in this compound, the presence of water in the pure salt was shown qualitatively.

DETERMINATION OF SELENIUM.—Several methods were tried, including the sulphur dioxide precipitation method, which yielded variable results owing to loss of selenium, and the one adopted was that of Benesch and Erdheim (*Chem. Ztg.*, 1930, **54**, 954; ANALYST, 1931, **56**, 133), in which the selenium is precipitated with hydrazine hydrochloride. Lehner and Kao (*J. Amer. Chem. Soc.*, 1925, **47**, 769; ANALYST, 1925, **50**, 255) state that to bring down selenium in the black form leads to errors, owing to occlusion both of solid impurities and of moisture which cannot be removed at 105° C., but, under the conditions to be described, this error does not appear appreciable.

A known quantity of cadmium selenate (about 0·1 grm.) was dissolved in 400 ml. of water containing 5 ml. of concentrated hydrochloric acid, and 20 grms. of hydrazine hydrochloride were added. The liquid was slowly heated to boiling, and kept boiling for half-an-hour. The black selenium was separated on a Gooch crucible, and washed, first with water, then with alcohol, and dried to constant weight at 105° C.

Selenium taken. Grm.	Selenium recovered. Grm.
0·0289	0·0288
0·0289	0·0288

If larger quantities of selenium are present (0·08 to 0·1 grm.), needing more reagent, occlusion occurs, and, if less hydrazine is employed, incomplete precipitation results.

DETERMINATION OF CADMIUM.—The method adopted was that of Berg (*Z. anal. Chem.*, **1927**, **71**, 321; ANALYST, 1927, **52**, 61), in which cadmium is precipitated as the 8-hydroxyquinoline ("oxine") complex. An advantage of using this reagent is that previous removal of selenium is unnecessary. The cadmium selenate (0·1 grm.) was dissolved in 100 ml. of water, the solution was made just acid (not more than 1 per cent.) with acetic acid, 5 grms. of sodium acetate crystals were added, and the cadmium was precipitated with a slight excess (15 ml.) of a 2 per cent. solution of "oxine" in alcohol (indicated by the yellow colour of the supernatant liquid). The mixture was heated to incipient boiling, and the precipitate was allowed to settle, filtered off on a Gooch crucible, washed first with warm and then with cold water, and dried to constant weight at 105° C.

Cadmium taken. Grm.	Cadmium recovered. Grm.
0·0435	0·0433
0·0435	0·0440
0·0411	0·0412
0·0411	0·0412

APPLICATION OF THE METHOD TO CADMIUM RED.—In the analysis of such pigments, the initial process of rendering soluble as much of the material as possible is of great importance, and the major constituents are preferably determined on one sample of the pigment.

Undissolved Residue.—One grm. of pigment, previously proved free from heavy metals other than cadmium, is transferred to a Kjeldahl flask with 40 ml. of water, and 40 ml. of concentrated nitric acid are added very slowly, with vigorous swirling. The reaction commences before warming, with the liberation of some sulphur and selenium, and, unless heating is prolonged, some of this sulphur and selenium may not be dissolved. The liquid is boiled down to about 20 to 30 ml., when another 15 ml. of concentrated nitric acid are added, and the liquid is again concentrated to 20 to 30 ml. Water is added, and the insoluble portion is filtered off, ignited and weighed. This residue is almost invariably tinted brown, but examination has shown that the colour is due solely to minute traces of impurity. The filtrate is evaporated to dryness to remove the nitric acid, distilled water is added, and the solution is made up to 100 ml.

Selenium.—Sixty ml. of the solution, diluted to 400 ml. with water, are made just alkaline with ammonium hydroxide, acidified with 5 ml. of concentrated hydrochloric acid, and the selenium is precipitated with hydrazine hydrochloride, as described above.

Cadmium.—Twenty ml. of the solution are diluted to 100 ml. with water, made slightly turbid with sodium carbonate, and cleared with a slight excess of acetic acid before precipitating with "oxine."

Sulphur.—The filtrate from the selenium precipitate is heated to boiling, treated with barium chloride in the usual way, and the sulphate is weighed as barium sulphate.

Water-soluble Material.—Five grms. of pigment are boiled for five minutes with 200 ml. of neutral distilled water, and the liquid is diluted to 250 ml. and filtered. The first 100 ml. of the filtrate are rejected, an aliquot part of the remainder is evaporated, and the residue is dried at 105° C.

Moisture.—For the moisture content, 0·5 grm. of pigment is dried for 1 hour at 105° C.

Free Sulphur.—Free sulphur is determined by extracting 5 grms. of pigment with boiling carbon disulphide under a reflux condenser.

TYPICAL ANALYSES.—Below are given typical analyses of two grades of pigment:—

	Cadmium Red.	
	"Light." Per Cent.	"Medium." Per Cent.
Undissolved matter (barium sulphate) ..	59·9	59·5
Volatile matter	0·2	0·2
Water-soluble matter	0·2	0·1
Free sulphur	Trace	Trace
Total cadmium	[28·7]	[18·9]
Selenium, calculated as CdSe	13·1	19·0
Residual cadmium, calculated as CdS ..	27·0	21·3
Total sulphur calculated as CdS ..	[26·0]	—
	100·4	100·1

SUMMARY.—A method is described for the complete analysis of cadmium red pigments, wherein the selenium is precipitated by hydrazine hydrochloride, and the cadmium as an 8-hydroxyquinoline complex. This use of hydroxyquinoline is permissible only if other heavy metals are absent—which was found to be the case with all the samples of cadmium reds examined. As a check on the methods, analytical figures for cadmium selenate are given.

I wish to thank the Government Chemist, Sir Robert Robertson, for permission to publish this note.

GOVERNMENT LABORATORY,
LONDON.

The Determination of Unsaponifiable Matter with special Reference to Fish and Marine Animal Oils

BY E. R. BOLTON, F.I.C., M.I.CHEM.E., AND K. A. WILLIAMS, B.SC., A.I.C.

IN describing an investigation into the halogen absorption of unsaponifiable matter which enabled us to classify the oils and fats into four groups (ANALYST, 1930, 55, 5) we published a method for the extraction of the unsaponifiable matter by means of petroleum spirit. This method may be applied to the majority of oils and fats with highly satisfactory results, as the removal of unsaponifiable matter is usually complete in the three extractions specified and the product obtained is not contaminated with soap, fatty acids, or unsaponified oil.

It is, however, recognised that the method is not suitable, as it stands, for use with fish or marine-animal oils, as the extraction in such cases may not be complete. We have suggested that the remedy lies in increasing the number of times the saponified oil is extracted, and have ourselves obtained satisfactory results by this means in many cases, but the extra time and manipulation involved have forced us to return to the use of ether as the extracting solvent.

The use of ether under certain conditions may lead to difficulties as great as those arising from the use of petroleum spirit, and the results obtained by its use in the past have lacked that precision and certainty which are required in analysis. This, in our opinion, has been due to the following:—

(i) Unless the conditions of the extraction are carefully controlled, three extractions with ether are not always sufficient for complete separation of the unsaponifiable matter;

(ii) The extract is invariably contaminated, to a considerable extent, with soap, which is difficult to remove completely.

A satisfactory method must, therefore, ensure that:—

(1) saponification of the oil is complete;

(2) the soap solution produced is alkaline, liquid, and not viscous;

(3) the proportions of soap, water and alcohol in this solution are such as to ensure that separation from the ether takes place quickly and completely without interference from emulsions;

(4) the proportion of ether which dissolves in the soap solution be as small as possible;

(5) the concentration of the soap and alcohol allows complete separation of the unsaponifiable matter in three extractions;

(6) the removal of soap, and products of its hydrolysis, from the ether extract be complete, or that it must be possible to determine the quantity remaining and allow for this in the weight of unsaponifiable matter obtained.

As a result of a long series of experiments we have concluded that the following conditions of experiment fulfil these requirements, and that departure from them to any material degree is liable to lead either to incomplete extraction or to contamination of the product.

METHOD OF DETERMINATION.—From 2 to 2·5 grms. of the oil are saponified by boiling under a reflux condenser with 25 c.c. of $N/2$ alcoholic potash for 1 hour. The flask is then removed from the condenser and its contents transferred to a separating funnel; the flask is washed out with 50 c.c. of water, which are added to the soap solution in the funnel. When the aqueous alcoholic soap solution has cooled somewhat it is extracted three times with 50 c.c. of methylated ether, the flask being rinsed with the ether before this is added to the contents of the separating funnel. The three extracts are combined in a second separating funnel and allowed to stand for a few minutes to enable any of the soap solution, which may have been mechanically carried over, to separate; this is drawn off, and the combined extracts are washed three times with 20 c.c. of $N/2$ aqueous sodium hydroxide solution and twice with water. In conducting the second and third washings with alkali and the two washings with water, the extract and washing solution are violently shaken. In general, emulsions will not form, although some trouble has been experienced with fats containing large proportions of saturated acids, because of the low solubility of the sodium salts; in such cases it is preferable to wash with *N*/2 potassium hydroxide rather than with *N*/2 sodium hydroxide solution. After washing, the extract is filtered into a weighed flask; the second separating funnel and filter being carefully rinsed with ether which is added to the main extract. The ether is evaporated off, and the flask and its contents are dried for 10 minutes in a water-oven, allowed to cool, and weighed.

The contents of the flask are then dissolved in warm neutral alcohol and any fatty acid present is titrated with *N*/10 sodium hydroxide solution, using phenolphthalein as indicator. The weight of fatty acid found (calculated by means of the expression 1 c.c. of *N*/10 sodium hydroxide solution is equivalent to 0·0282 grm. of fatty acid) is deducted from the weight of crude unsaponifiable matter. The correction to be applied in this manner rarely exceeds 2 mgrms.

The quantities specified in the method must be strictly adhered to, as any material departure therefrom leads to serious difficulties.

The procedure described above has been the standard practice in this laboratory for well over a year, with entirely satisfactory results.

THE LABORATORY,
6, MILNER STREET, CHELSEA, S.W. 3.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

A NEW METHOD OF PREPARING A PICROLONATE FROM A PICRATE AS A MEANS OF IDENTIFICATION

IN the course of some biochemical investigations carried out here, it became necessary, for purposes of identification, to convert indolethylamine picrate into the corresponding picrolonate. The usual methods of bringing about the interconversion by way of the hydrochloride or sulphate failed, owing to (1) the difficulty of hydrolysing the very insoluble indolethylamine picrate by means of hydrochloric or sulphuric acid, and (2) the ease with which soluble salts of indolethylamine decompose on evaporation, giving resinous products. The method used by Dudley, Rosenheim and Rosenheim (*Biochem. J.*, 1924, **18**, 1268) for converting spermine picrate into the hydrochloride, when applied to the present case, was also unsatisfactory.

The following new method of converting a picrate into a picrolonate, involving the use of nitron, and depending on the extreme insolubility of nitron picrate (1 in 250,000; *cf.* Busch and Blume, *Z. angew. Chem.*, 1908, **21**, 354; Cope and Barab, *J. Amer. Chem. Soc.*, 1917, **39**, 504) is described in the hope that it may be extended and prove useful to other workers.

A quantity of 0·35 grm. of indolethylamine picrate (m.pt. 243–244° C., with decomposition; picric acid determined by means of nitron 58·0, 58·2; calc. 58·8 per cent.) was dissolved in 250 c.c. of boiling water containing 3 c.c. of 2 *N* sulphuric acid, and a solution of 0·27 grm. of nitron in 4 c.c. of 5 per cent. acetic acid was added to the picrate solution previously cooled to 60° C. The mixture was cooled, filtered from nitron picrate, and the filtrate was treated with 0·22 grm. of picrolonic acid dissolved in a little warm alcohol. After standing overnight a very small quantity of a sticky precipitate separated and was rejected. The clear liquid was concentrated *in vacuo* below 40° C. to 100 c.c. and cooled. The crystals which separated were recrystallised from hot water, giving deep yellow crystals of indolethylamine picrolonate, melting at 229–230° (decomp.). Ewins (*J. Chem. Soc.*, 1911, 99, 270) gives 231° C. as the m.pt. of this compound. (Found by microanalysis: N = 18·8 per cent. Calc. for $C_{10}H_{12}N_2.C_{10}H_8N_4O_5.H_2O$: N = 19·0 per cent.)

We wish to express our thanks to the Medical Research Council for a grant which has enabled one of us (L. K.) to participate in this work.

Louis Klein and John F. Wilkinson.

The Department of Clinical Investigations and Research,
(The University of Manchester),
The Royal Infirmary, Manchester.

FLUORESCENCE IN RELATION TO SEWAGE

Several hundred effluents and sewages, and also sludges in various stages of digestion, have been examined in filtered ultra-violet light to determine whether there is any correlation between the fluorescence and any of the numerical results obtained by chemical analysis. The source of light used was the Hanovia quartz mercury vapour lamp, fitted with a light filter which allows only wave-lengths around 3650 Å.U. to pass.

Sewages, raw and partly treated, and effluents all give a blue fluorescence, due partly to suspended, and partly to dissolved substances. The intensity of the fluorescence is increased in alkaline solution, but practically disappears in acid solution.

The intensity of the fluorescence appears to have no connection with the oxygen absorption (4-hours' figures) of shaken samples. A comparison between the free and albuminoid ammonia figures and the intensity of the fluorescence of shaken, filtered or settled liquids, showed that there is apparently no connection between them.

A substance which is very strongly fluorescent can be extracted with ether from raw shaken sewage. It cannot be extracted with carbon tetrachloride, and it does not come over on distillation with steam. After evaporation of the ether two layers are obtained—a scum which fluoresces with a very intense reddish-yellow colour, and a liquid showing an intense reddish-blue fluorescence. The scum appears to be of a fatty nature, and is only partly saponifiable. The residue left on evaporation of the ethereal extract gives Reif's fluorescence test for creatinine, and a few chemical tests also pointed to the presence of this substance.

Titration of raw sewages in ultra-violet light, with fluorescein as a fluorescent indicator, has no advantage over the usual method of titration with methyl orange as indicator. With the capillary-strip method of Danckwortt and Pfau no zones, except a thin white fluorescent edge, were obtained. Stains produced by hydrogen sulphide on lead acetate paper appear a little darker under the lamp than in daylight.

Fresh crude sludge appears very dark under the lamp, and shows a faint greenish-grey fluorescence with a number of intensely fluorescent specks, blue, yellow and green in colour. The spots, which appear to be due to particles of fat and cellulose, gradually disappear as the digestion of the sludge proceeds, a fully digested sludge being practically free from them. Here, again, the lamp does not offer any advantage over the usual methods for determining the stage of digestion. A fatty substance which can be extracted from dried sludge with carbon tetrachloride gives an intense yellowish-brown fluorescence under the lamp.

Further experiments are in progress on the fluorescence of the flora and fauna of the filter beds, but, so far as my experience goes, the claims made for fluorescence analysis cannot be extended to the examination of sewage.

I have to thank Mr. A. S. Miller, M.Sc., A.I.C., for suggestions in connection with this work, and Mr. A. S. Parsons, M.Inst.C.E., Borough Surveyor, for facilities for undertaking the investigation and permission to publish this note.

J. A. RADLEY.

READING CORPORATION SEWAGE DISPOSAL WORKS,
MANOR FARM, READING.

Official Appointments

THE Minister of Health has confirmed the following appointments:

ALBERT EDWARD PARKES, F.I.C., as Public Analyst for the County Borough of West Ham (January 1st, 1932).

HAROLD LOWE, M.Sc., F.I.C., as Public Analyst for the County Borough of Chester (January 5th, 1932).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE THIRD QUARTER, 1931

OF the 1185 samples examined during the quarter, 57 were bought formally and 1128 informally. The 25 incorrect food samples included 19 milks, 2 of vinegar, and 1 each of ginger, brandy wine, cream ice, and sugar confectionery; there were also 6 incorrect samples of drugs.

MILK ADULTERATION AND THE FREEZING-POINT TEST.—The percentage of milk samples adulterated or below the minimum limits was 3·0 per cent., as compared with 6·8 per cent. and 4·7 per cent. for the corresponding quarters of 1929 and 1930. This may be partly due to the publicity given to a Court case in which the freezing-point method was introduced for the first time. In many cases it has been found possible to use, as a basis for calculation, the freezing-point of a farm sample taken in connection with a case, thus increasing the accuracy of the calculation. Thus, in the case referred to above, two samples were taken, respectively, from a serving can and from a churn loaded on a lorry. Both were proved to contain added water (the amount in the sample from the churn being 24 per cent.) by means of the evidence afforded by the freezing-point test and the presence of nitrates. A sample of the mixed milk taken at the vendor's farm was of very good quality, and had a normal freezing-point. A fine of £10 in respect of each sample was imposed.

Extra Cream Ice.—Twelve samples of ice cream and cream ice were examined. They contained from 2 to 24 per cent. of butter fat, and, in view of there being no standard for ice cream in this country, all but one were passed as genuine. This last sample was described as "Extra Cream Ice," and contained only 2 per cent. of fat. It was returned as being falsely labelled, since 2 per cent. is the minimum amount for ice cream, and cream ice should, presumably, contain more fat than ice cream. One would expect "Extra Cream Ice" to be unusually good.

Vinegar.—One of the 17 samples examined consisted of artificial vinegar. At present it is difficult to prosecute a vendor for the sale of artificial vinegar for vinegar, for the retailer is usually unaware of the nature of the article supplied to him in many cases as "pure vinegar," and it is almost impossible to purchase a sample as "vinegar" in course of delivery from the wholesale dealer. It is to be hoped that the Committee which is to consider food standards and definitions will make some attempt to distinguish artificial vinegar from vinegar.

Mineral Matter in Sugar Confectionery.—A sample sold under the name of "Munchies," consisted of rather expensive sweets of an unusual type. They contained an inner mass of chocolate, etc., and had an outer coating of sugar, chalk and French chalk, resembling that of a pill. The total amount of mineral matter was 10·3 per cent., including 6·3 per cent. of chalk and 3·4 per cent. of talc.

H. H. Bagnall.

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

LABELLING OF POISONS

On November 26th, 1931, the Council of the Pharmaceutical Society sued a grocer at Brentford County Court for penalties for infringement of the Poisons and Pharmacy Act, 1908. Mr. Glyn Jones, for the plaintiffs, said that the defendant, who was not a registered chemist or druggist, admitted the sale of a bottle of Izal, which was included in the Schedule to the Poisons and Pharmacy Act, 1908, as a poison. A compound containing less than 3 per cent. of homologues of carbolic acid might be sold by grocers, but if it contained more than that quantity it could not be sold unless it was described as being sold for special purposes. In this case it was described as a sheep wash, and for agricultural and horticultural purposes, and for disinfecting utensils, and was properly labelled "poison." The question was whether this was a preparation sold as sheep wash only, or for purposes in agriculture, and bearing a label, giving notice that it was sold for the special purposes for which it was produced. The Society contended that this was an attempt to convert what was essentially prohibition into encouraging the sale of a poison by other than qualified druggists. The manufacturers had suggested that this case should be tested in a friendly spirit. They put up Izal in two bottles, one for pharmacy and the other for general use, but the bottles were similar and could not be distinguished at a distance. The contents were the same, and that labelled for agricultural purposes could be sold anywhere. In his (counsel's) opinion, a sale for general purposes in agriculture was wrong, and the compound could only be sold for special purposes, which must be disclosed on the label.

Mr. C. E. Corfield, B.Sc., F.I.C., said that he had analysed the contents of the bottle in question, and that it contained 39·1 per cent. of phenols, and not less than

30 per cent. of the homologues of carbolic acid. He had also analysed the contents of one of the tins sold by grocers, and they had the same composition as the contents of the bottles.

Dr. Bernard Dyer, F.I.C., said that compounds other than Izal were used in agriculture, and that the label on every bottle must specify the method of use approved by the Minister of Agriculture. That did not appear on the bottle in question. As a soil disinfectant it would be of little use, and, if applied to a shrub or tree in leaf, according to the proportions given, it would be injurious; if used in the winter it would not be strong enough. The use of phenol preparations for soil sterilisation had now been mainly substituted by that of formaldehyde. It would make a good sheep dip if about twenty-five bottles were used to an ordinary "bath," and it might be useful on poultry farms for disinfecting hen roosts, etc. For ordinary disinfectant purposes it would be excellent. Mr. T. Tickle, B.Sc., F.I.C., agreed with the evidence of Dr. Dyer.

Mr. Norman Birkett, K.C., for the defence, said that the defendant's reply to the charge was that what he did came within the exceptions to the Act of 1908. To come within those exceptions a compound must be labelled "poison," must be in a closed vessel, and must bear the name of the maker. All these were complied with, but it was claimed that the label did not specify the special purposes for which the preparation could be used. If it were sold as a sheep wash and a farmer used it for other purposes, the vendor could not be to blame. As to the public point of view, if the contents of the bottle were diluted to 3 per cent. of the homologues of phenol it might be sold by a grocer, and the public, thinking that it was then the same article as sold by a druggist, would be deceived.

Mr. Glyn Jones, replying, said that ever since 1868 the legislature had required that poisons as a class must be sold only by qualified persons, and it was not intended that goods just on one side of the line should be sold as non-poisonous by the use of a label. Could a poison be less a poison because the packet bore the words: "It could be used as sheep wash"? The Schedule should not be evaded in that way. There must be a statement on the label that the bottle was sold for special use, and not for general use, and there was no evidence that the defendant sold agricultural or horticultural goods.

His Honour, Judge Higgins, said that the Act exempted preparations for sheep wash and for purposes of agriculture and horticulture, and he thought that the label covered the sale in this case. It was quite clear that agricultural and horticultural purposes included the washing of pans, disinfecting of premises, and cleansing of vessels, all of which must form part of agricultural work. He thought the Act had omitted something. It should have added the words: "It must not be used for any other purpose than those specially stated."

Judgment was given for the defendant, with costs.

General Medical Council

PHARMACOPOEIA COMMISSION

REPORTS OF SUB-COMMITTEES*

IN addition to the Reports of the Pharmaceutical Chemistry Sub-Committee and of the Cod-liver Oil Colour Test Sub-Committee (*cf.* ANALYST, 1931, **56**, 457), the following Reports have been issued:

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* The Reports may be obtained from the General Medical Council, 44, Hallam Street, London, W.1. Prices: No. 1, 1s.; Nos. 2 and 3 together, 3s.; No. 4, 1s. 6d.; No. 5, 1s.; No. 6, 1s. 6d.; No. 7, 1s.; No. 8, 1s. 6d. Criticism of the recommendations is invited.

REPORT OF PHARMACY SUB-COMMITTEE, AUGUST, 1930. (No. 1.)

This Sub-Committee suggests new formulae for certain preparations to be added to the Pharmacopoeia, and makes recommendations relating to the manufacture of some which require alteration. The subjects dealt with include Acids, Alcohol, Confections, Effervescing Preparations, Extracts and Liquid Extracts, Glycerins, Infusions, Liniments, Lozenges, Mucilages, Ointments, Oxymels, Plasters, Powders, Resins, Solutions, Spirits, Suppositories, Syrups, Vinegars, Waters (Aromatic), and Miscellaneous Preparations. The Sub-Committee recommends that Industrial Methylated Spirit should be described in the Pharmacopoeia, and that, subject to the statutory regulations, its use in making solid extracts and certain other preparations should be permitted.

REPORT OF THE SUB-COMMITTEE ON DIGITALIS AND STROPHANTHUS, MAY, 1931. (No. 4.)

The Sub-Committee makes recommendations for the preparation of tincture and infusion of digitalis and of tincture of strophanthus, and puts forward proposals for the biological standardisation of these drugs. Comment is invited on these proposals.

REPORT OF THE SUB-COMMITTEE ON THE PREPARATION OF STERILE SOLUTIONS FOR INJECTION, 4TH MAY, 1931. (No. 5.)

The Sub-Committee was appointed to prepare for the Commission a general statement of the principles to be adopted in sterilising solutions, and to supply notes on the best methods of sterilising the solutions of special drugs, which could be appended to the monographs on these drugs in the Pharmacopoeia. The recommendations cover the sterilisation of glass vessels and containers, heating in an autoclave, Tyndallisation, filtration, sterilisation of oily solutions, and an emergency method of sterilisation. The methods most suitable for certain specific drugs are given. The report deals also with the preparation of sterilised distilled water and of physiological saline solution.

SECOND REPORT OF PHARMACY SUB-COMMITTEE, MAY, 1931. (No. 6.)

This Report presents a résumé of the Sub-Committee's recommendations on the preparation of the following articles for inclusion in the new Pharmacopoeia:—Collodion, Elixir Cascarae Sagradae, Liquid Extract of Liver, Dry Extract of Liver, Dry Extract of Hyoscyamus, Eye Ointments, Hydrargyrum *cum* Creta, Concentrated Infusions, Injections, Liniments, Oxymels, Pills, Powders (for which a system of description based on coarseness or fineness is proposed), Solutions, Spirit of Nitrous Ether, Suppositories, Syrups, and Tincture of Stramonium.

REPORT OF SUB-COMMITTEE ON AMPOULE GLASS, JUNE, 1931. (No. 7.)

Glass containers of medicinal solutions should yield but little alkali to the solutions contained in them, and two tests are recommended for determining the limit of alkalinity. (1) *Applied to the glass when crushed.*—The apparatus to be used is first tested by placing the test solution (100 ml. of water, 0·4 ml. of 0·01 *N* hydrochloric acid, and 0·4 ml. of a strong solution of methyl red, made by dissolving 0·04 grm. of methyl red in 50 ml. of 95 per cent. alcohol, adding 1·5 ml. of 0·05 *N* sodium hydroxide solution and water to 100 ml.) in a vessel of resistant glass, transferring the solution, while boiling, to a 250 c.c. conical flask of resistant glass fitted with a reflux condenser, or with a simple condensing apparatus made by fitting a short wide tube of resistant glass (closed at one end and supplied with a flow of cold water) into the stopper of the conical flask. The whole is placed in a boiling water-bath, and at the end of 1 hour the red colour of the test solution should remain unaltered; otherwise, the flask and condenser are unsuitable for the test. Five grms. of the ground glass (particles passing a No. 25, but not a No. 36 sieve) are washed free from dust with 95 per cent. alcohol in a small conical flask, and dried at 100° C., and 100 ml. of fresh test solution are added, the condenser is inserted and the contents of the flask are boiled for half-an-hour, when the colour should not have changed from pink to the full yellow of methyl red, as indicated by comparison with a solution prepared by adding to 10 ml. of the test solution 0·1 ml. of 0·1 *N* sodium hydroxide. (2) *Ampoules.*—Not less than 6 ampoules are filled to their prescribed capacity with acid solution of methyl red (8·3 ml. of 0·02 *N* hydrochloric acid and 20 ml. of strong solution of methyl red as above, made up to 1000 ml.) sealed and heated in steam at a pressure of 15 lbs. per sq. in. for half-an-hour. After cooling, the pink colour should show no change on comparison as described above. The tests should, if possible, be carried out not more than 14 days before the ampoule is to be used, and, if stored ampoules do not respond to the test, they should be re-tested after washing internally with a 5 per cent. (v/v) solution of acetic acid, followed by 3 washings with water, provided that, if the ampoules then pass the test, this washing is carried out before they are brought into use.

D. G. H.

REPORT OF SUB-COMMITTEE ON ERGOT, OCTOBER, 1931. (NO. 8.)

The conclusions reached by the Sub-Committee are that ergotoxine is to be regarded as the active principle for which ergot preparations are administered; that the colorimetric method carried out as recommended permits of an accurate determation of total alkaloid in ergot, and its liquid extract; that the colorimetric method has advantages over gravimetric methods in requiring smaller amounts of material and less time; and that the margin of error in biological methods is at least as great as that due to the variation in the relative proportion of ergotoxine and ergotinine in the total alkaloid. Since the variation in the alkaloidal content of ergot of rye is wide, the standard for the alkaloid in the liquid extract is important, and it is recommended that it should be 0·05 per cent. of total alkaloid ±0·01. The strength of the official extract is recommended as corresponding with 0·03 per cent. of ergotoxine, and, since the evidence before the Sub-Committee suggests that 60 to 70 per cent. of the total alkaloid consists of ergotoxine, this percentage is equivalent to a total alkaloid percentage of 0·05, measured by the colour test. The M. I. Smith colour test for ergot is capable, particularly in its slightly modified form, of giving results which agree closely in the hands of different workers. The ether must be free from peroxide; and, although hydrochloric acid may be used instead of sulphuric acid, traces of peroxide affect the test to a greater extent, and the sulphuric acid method is recommended for official adoption.

Sulphuric Acid Method.—Five grms. of ergot, in No. 60 powder, are extracted with cold petroleum spirit (b.pt. 40–50° C.), and, when the fat is completely removed, the extracted drug is dried at a temperature not exceeding 30° C., and 100 ml. of anaesthetic ether are added. After standing in a stoppered glass for 10 minutes, 0·5 grm. of light magnesium oxide, diffused in 20 ml. of water, is added, and the mixture is shaken at intervals during 30 minutes. Powdered tragacanth (1·5 grm.) is then put in, and, after shaking, 50 ml. (2·5 grms. of drug) are filtered through cotton wool, and shaken in a separator with 4 successive 10-ml. portions of a 1 per cent. (w/v) solution of tartaric acid in water. The aqueous liquids are separated and mixed, the dissolved ether is evaporated, and water is added to suitable volume (say, 40 ml.), and to 2 ml. of this solution is added with constant shaking, and drop by drop, with cooling arrangements, 1 ml. of a solution of dimethylamino-benzaldehyde (0·25 per cent., w/v, in sulphuric acid). The mixture is exposed to bright light until the blue-violet coloration reaches a maximum. A standard for comparison is made at the same time and in the same way by adding to 2 ml. of a freshly-prepared 0·006 per cent. (w/v) solution of ergotoxine ethane sulphonate in 1 per cent., w/v, tartaric acid, 1 ml. of solution of dimethyl-amino-benzaldehyde. Quantities are so arranged that the acid solution of alkaloids is diluted to produce a colour very close to that of the standard. The proportional intensities allow of the calculation of the amount of alkaloid. If the liquid extract of ergot is to be assayed, 5 ml. are treated with 50 ml. of water, rendered slightly alkaline with ammonia, and extracted with 40, 25, 20 and 10 ml., successively, of anaesthetic ether, the united extracts are washed with 25 ml. of water mixed with 0·2 ml. of dilute ammonia and then with 25 ml. of water, and the treatment with tartaric acid is carried out as above.

The Hydrochloric Acid Method.—This needs no precautions as to heat. To 5 ml. of liquid extract are added 20 ml. of a 1 per cent. (w./v.) solution of sodium bicarbonate (the mixture should be alkaline to litmus), and the mixture is extracted with 40, 25 and 15 ml. of anaesthetic ether. The united extracts are washed with 10 ml. of a 1 per cent. solution of sodium bicarbonate, and the ethereal solution is extracted with 15 ml. of a 1 per cent. (w/v) solution of tartaric acid. The acid layer is drawn off, and the extraction is repeated twice with 10 ml. of acid. The dissolved ether is removed from the united acid liquids, which are made up to a suitable volume, and the colour test is applied as before, the hydrochloric acid reagent being used.

D. G. H.

Dominion of Canada

REPORT OF THE DOMINION CHEMIST FOR THE YEAR ENDING MARCH 31st, 1930

In his Annual Report, Dr. F. T. Shutt points out that, as in the past, the work of the Division of Chemistry of the Department of Agriculture has been carried forward with two main functions in view: the investigation of problems affecting Canadian agriculture and the assistance of farmers, through correspondence and by analytical work, in matters related to soils, manures, feeding stuffs, well waters, etc.

In addition to these two main branches of work, the Division officially examines and reports on meat and canned foods and other packing-house products from the Health of Animals Branch; canned, preserved and fresh fruits from the Fruit Branch; condensed and evaporated milks, milk and cream powders, etc., from the Dairy and Cold Storage Branch.

Further, the division has rendered chemical assistance to the following branches of the Government service: Customs and Excise Branch, Department of National Revenue, National Parks Branch, Department of the Interior, Entomological Branch, Live Stock Branch, Seed Branch, Department of Agriculture, Department of National Defence, Public Printing and Stationery Department, Marine and Fisheries Department.

The number of classified samples received for examination during the year was 5,451, approximately 1200 more than during the preceding year. A comparison of the tables for the two past years shows that there has been an increase in every branch of the Division's activities, with the exception of well waters—the most marked increase being in the phase of work dealing with cereals, feeding stuffs and forages. The subjects specially investigated include the following *inter alia*:—

Spent Bone Char.—During the past five years the spent bone char from the clarifying of raw sugar, which was formerly used solely as a phosphatic fertiliser, has been employed in stock feeding as a "mineral" adjunct to the ration to furnish lime and phosphoric acid, necessary elements for bone and tissue building in the animal. It has been further suggested that bone char, by reason of its porous character and the presence of charcoal, may be useful in the animal economy in regulating or, perhaps, in preventing intestinal disturbances. The bone phosphate content ranges from 72 to 82 per cent., and is from 20 to 30 per cent. higher than that found in edible bone meals.

IMPORTED COLOURS FOR PEAS.—Three samples of imported colours for peas were examined. One sample was naphthol green B (S & J 398), a non-permissible coal-tar dye. The other two samples contained natural colouring matter. One of these samples—a dark green liquid—contained 0·25 per cent. of copper.

SPECIAL JAM INVESTIGATION.—With a view to the establishment of new standards for jams, several samples of strawberry, raspberry and cherry jams, and of the syrups used in their preparation were examined.

The average, maximum and minimum percentages of water-soluble solids (determined by difference) in forty-five samples of strawberry jams were 71·1, 80·3 and 64·8, respectively.

The average, maximum and minimum water-soluble solids (determined by difference) in ten samples of raspberry jam were 71·9, 76·3 and 65·8, respectively.

The average, maximum and minimum water-soluble solids (determined by difference) in eight samples of cherry jams were 73·1, 77·2 and 69·8, respectively.

A summary of results of analyses of seventeen samples of syrups used in the preparation of these jams is given in the following table:

SUMMARY OF RESULTS OF ANALYSES OF SYRUPS USED IN THE PREPARATION OF JAMS

	Total sugars. Per Cent.	Sucrose. Per Cent.	Invert sugar. Per Cent.
Average	67·1	51·1	16·0
Maximum	68·0	54·9	25·9
Minimum	66·5	40·7	12·7

Four samples of strawberries used in the preparation of strawberry jams were analysed. The results of analyses were as follows:

ANALYSES OF STRAWBERRIES USED IN THE PREPARATION OF STRAWBERRY JAMS

Variety.	Total solids. Per Cent.	Water-insoluble solids. Per Cent.	Total sugars (as invert). Per Cent.	Pectin (as calcium pectate). Per Cent.	Ash. Per Cent.	Acidity (as citric acid). Per Cent.
	9·34	2·27	3·64	1·20	0·64	1·53
Aroma ..	9·86	1·62	3·92	0·98	0·72	0·89
Aroma ..	10·26	2·31	4·34	1·34	0·62	1·08
	9·41	2·42	3·53	0·72	0·81	1·14

PRESERVATION OF EGGS WITH "DRY ICE."—It has been shown that one factor in the deterioration of eggs on storage is the loss of carbon dioxide. It therefore seemed probable that eggs would keep better if this loss of carbon dioxide was prevented by keeping the eggs in an atmosphere containing a small percentage of carbon dioxide.

In co-operation with the Poultry Division of the Livestock Branch a preliminary investigation was carried out in these laboratories to determine whether or not the storage of eggs in an atmosphere of carbon dioxide by enclosing them in sealed boxes containing "dry ice" (solid carbon dioxide) would assist in their preservation, and to ascertain how much "dry ice" would furnish the best results for keeping eggs during the summer for ten to fifteen days. The results seemed to show that even quite small percentages of carbon dioxide influenced the keeping qualities. It was found that 30 dozen eggs, which were kept in a vaseline-sealed metal container for twelve days, showed very little visible deterioration at the end of this period. The percentages of carbon dioxide in the container at the beginning and end of the period were determined and found to be 0·05 and 0·28 per cent. by volume, respectively.

FERMENTATION IN CANADIAN HONEY.—The Canadian honey industry has suffered considerable losses through the spoilage of honey on storage by fermentation. This fermentation is caused by sugar-tolerant yeasts, several types of which have been isolated and studied by the Division of Bacteriology of the Central Experimental Farm.* Infection by these organisms may be due, in part, to careless handling, and, in part, to the transportation by the bee of yeasts from the flowers to the comb. In so far as the infection is due to careless handling it can be avoided; in so far, however, as it is due to the bees themselves it cannot be avoided, and, therefore, some control measure is necessary in order that the activity of the yeasts may be kept at a minimum.

In order to obtain an insight into the conditions most favourable to the growth of yeasts in honey the following investigation was undertaken by the Division of Chemistry in co-operation with the Divisions of Apiculture and Bacteriology. Two hundred samples of honey, collected from all parts of Canada, were sent to the Division of Apiculture. There, each sample was divided into two parts, one of which was placed in a hermetically sealed receptacle and stored at room temperature, whilst the other was sent to the Divisions of Bacteriology and Chemistry for bacteriological and chemical examination.

At the time of the publication of this Report 122 samples of the series had been analysed, and the results are summarised in the following tables:

MOISTURE, PER CENT.

	15–15·9.	16–16·9.	17–17·9.	18–18·9.	19–19·9.	20–20·9.	21–22.
Number of samples	1	19	35	50	14	2	1
Percentage of samples	1	15·0	28·5	41·0	11·0	1·5	1·0

ASH, PER CENT.

	0·02–0·039.	0·04–0·059.	0·06–0·079.	0·08–0·099.
Number of samples	19	52	20	12
Percentage of samples	16	43	16	10
	0·10–0·139.	0·14–0·199.	0·20–0·299.	0·331.
Number of samples	6	5	5	1
Percentage of samples	5	4	4	1

TITRATABLE ACIDITY.

(c.c. of *N* sodium hydroxide solution per 100 grms. of honey.)

	10–14·9.	15–19·9.	20–24·9.	25–29·9.	30–36.
Number of samples	40	47	23	4	8
Percentage of samples	33·0	38·5	19·0	3·0	6·5

HYDROGEN ION CONCENTRATION.

(Grm.-ions per litre $\times 10^{-5}$.)

	39·8.	32–16.	16–8.	8–4.	4–2.	0–2.
Number of samples	2	38	50	25	7	1
Percentage of samples	2·0	31·0	40·5	20·0	5·5	1·0

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* Bull. No. 116, New Series, Dept. of Agriculture.

Nitrogen, per Cent.

	0·019.	0·020–0·024.	0·025–0·049.	0·050–0·074.
Number of samples	1	9	88	2
Percentage of samples	1·0	8·5	83·5	2·0

	0·075–0·099.	0·100–0·125.	0·156.
Number of samples	2	2	1
Percentage of samples	2·0	2·0	1·0

Invert Sugar, per Cent.

	70–71·9.	72–73·9.	74–75·9.	76–77·9.	78–79·0.
Number of samples	4	21	49	40	8
Percentage of samples	3	17	40	33	7

Sucrose, per Cent.

	0·0.	0·1–0·9.	1·0–1·9.	2·0–2·9.	3·0–3·9.
Number of samples	15·0	16	36	22	14
Percentage of samples	12	13	30	18	11

	4·0–4·9.	5·0–5·9.	6·0–6·9.	7·0–7·9.	8·0–8·9.
Number of samples	10	5	1	2	1
Percentage of samples	8	4	1	2	1

Laevulose, per cent.

	37–38·9.	39–40·0.	41–42·9.	43–44·9.	45–47.
Number of samples	7	48	52	13	2
Percentage of samples	6	39	42	11	2

Ratio of Laevulose to Dextrose.

	0·95–0·99.	1·00.	1·01–1·09.	1·10–1·19.
Number of samples	1	3	25	41
Percentage of samples	1	3	24	40

	1·20–1·29.	1·30–1·39.	1·40–1·49.	1·72.
Number of samples	22	9	1	1
Percentage of samples	21	9	1	1

Analyses of Samples of Honey which Fermented when Stored at Room Temperature

No.	Moisture.	Invert sugar.	Sucrose.	Laevulose.	Dextrose.	Ash.	Nitrogen.	Titratable acidity. *N* NaOH per 100 grms. honey.	*p*H.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	c.c.	
1.	19·3	76·0	1·0	38·6	38·5	0·253	0·097	31·5	4·5
2.	20·2	74·3	1·8	40·9	34·8	0·044	0·034	15·0	3·9
3.	22·4	70·3	1·0	39·1	32·6	0·058	0·036	20·8	4·1
4.	21·6	70·3	0·0	38·4	33·2	0·075	0·086	35·4	4·1
5.	19·5	76·8	0·0	40·9	36·2	0·072	0·040	22·4	3·6
6.	19·9	76·5	1·2	40·2	36·7	0·195	0·042	22·7	3·7

Analyses of Samples of Honey in which Fermentation is Suspected

No.	Moisture. Per Cent.	Invert sugar. Per Cent.	Sucrose. Per Cent.	Laevulose. Per Cent.	Dextrose. Per Cent.	Ash. Per Cent.	Nitrogen. Per Cent.	Titratable acidity. N NaOH per 100 grms. honey. c.c.	*p*H.
1.	18·9	72·4	1·7	43·8	30·3	0·166	0·046	17·7	3·8
2.	19·3	76·2	0·0	42·0	35·6	0·039	0·048	18·8	3·0
3.	19·9	76·1	0·3	43·4	34·5	0·048	0·034	14·5	3·7

By comparing the analyses given in the tables above with the summary of the analyses of Canadian honeys given in the preceding tables it will be seen that the average moisture of the fermented samples is definitely higher than the average moisture of Canadian honeys. This substantiates the conclusion of a previous investigation, *viz.* that a high moisture content in honey is favourable to fermentation. In the case of some of the other constituents, as, for example, nitrogen, titratable acidity, and ash, there is sufficient variation from the general average to suggest that they, too, might play a part in determining the optimum conditions for fermentation. Until the investigation is completed, however, it would be dangerous to draw any definite conclusions other than those just intimated.

Palestine

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1930

THE Government Analyst (Mr. G. W. Baker, F.I.C.) reports that 6359 samples were examined, including foods, drugs, waters, minerals, and supplies under Government food contracts.

MILK.—There was a decrease in the number of prosecutions for adulterated milk (standard: fat, 3 per cent.; solids-not-fat, 8·0 per cent.), but some of this decrease is attributed to an increase in subterfuge on the part of the vendor, helped probably by the common tendency to take samples at fixed times. One difficulty is that much of the milk sold by street vendors is from individual animals and very small herds of three or four cows, or is the mixed milk of cows, goats and sheep.

SEMNEH.—A high Polenske figure is not necessarily an indication of adulteration, as it may be due to the presence of goat butter (Atkinson, ANALYST, 1928, **53**, 520). There is a Customs duty on "mixed" (adulterated) semneh, but none on pure semneh of Syrian origin, and this has involved the examination of samples from every consignment. As a sorting test in this connection use has been found for the ultra-violet lamp. Incidentally, it has been found that the yellow fluorescence of milk is, apparently, not due to the fat, as suggested by Popp (ANALYST, 1926, **51**, 540). This is being investigated further.

ALCOHOL.—The Intoxicating Liquors Ordinance, 1927–30, specifies that "Arak" is spirits made from fruit and the anise plant by distillation. Cognac includes brandy and means spirits distilled from the fermented juice of grapes. Wine means any fermented liquor made from the juice of fresh grapes. Molasses and grain alcohols pay a higher duty than other spirits. After the 1931 vintage, grape alcohol alone is to be used for the fortification of sweet wines.

The addition of sugar other than that of the grape to wine is not permitted, and, in connection with an allegation that the addition of sugar was necessary for the manufacture of sweet wine in this country, samples of grapes were submitted by the Director of Agriculture. The sugar content of the juice ranged from 21 to 33 per cent.

CRIMINAL INVESTIGATION.—*Photography of Documents, etc.*—For the routine photography of documents, labels and other exhibits up to natural size, with the minimum of trouble, a special cabinet has been constructed. An opening in the top of this cabinet takes a folding hand camera resting vertically. The object is placed upon a movable platform in the cabinet, in which electric illumination is arranged. The exposure is controlled by the light switch and averages 30 seconds.

For taking comparison photographs on one plate of firing pin impressions in brass cartridge cases, two independent sources of illumination are used, and the intensity is varied to compensate for differences in the reflecting power of the object. Backed plates are used.

X-ray photography has been found useful for examining the internal structure of bullets without mutilation of the exhibits. In one murder case the character of the nose filling of bullets, as shown by *X*-ray photography, provided important evidence (see ANALYST, 1930, **55**, 738).

POISONING CASES.—Arsenic was detected in 72 cases, mercury in 5, and strychnine in 2 cases of animal poisoning.

In the anti-locust campaign of 1930, poison bait made of bran and sodium arsenite was distributed over large areas, especially in the Beersheba district. The question then arose whether there was any danger of contamination of water supplies collected from those areas during the rainy season. Arrangements were, therefore, made for the examination of samples taken after the first heavy rains. A sample of dead locusts and débris from a poisoned area was also examined. Of the 15 samples of water examined, one contained 0·2, one 0·1, and the rest less than 0·1 part per million, while the locust débris contained 0·05 per cent. of arsenious oxide. There is no doubt that many goats were poisoned by feeding in the affected area, but no case of human poisoning from locust bait came to the notice of these Laboratories.

Arsenic Sulphide as Poison.—In cases of criminal poisoning the arsenic is more often than not given in the form of artificial sulphide, which depends for its poisonous properties upon the amount of white arsenic it contains. Several specimens examined contained about 50 per cent. of arsenious oxide. In conjunction with lime this sulphide is used to make a depilatory preparation, and for that reason, no doubt, it is often at hand when there is any poisoning to be done. It is supposed that the natural sulphides, owing to their insolubility, are comparatively non-toxic, and this is supported by tests made in these laboratories on rats.

In one case, in which the Assistant Analyst was called to give evidence, traces of sulphide of arsenic had been found in the dust in the seams of the accused's pocket and 17·37 mgrms. of arsenic were found in 1880 grms. of viscera of the deceased. Most of this arsenic was found in the liver.

Other poisons.—Mercury is often administered as the oxide, which, apparently, has other domestic uses. Datura seeds obtained from the local thorn apple are generally crushed and inserted into figs. They are used as a narcotic to facilitate robbery.

COUNTERFEIT COINS.—The present Palestine currency was introduced into circulation in November, 1927, and in January, 1928, counterfeits of the new currency were submitted to these laboratories for examination. In all, 40 coins were examined during that year, of which 34 were confirmed as counterfeit. Very few have been submitted since.

The most obvious fault in the cast coins has generally been found in the milling. There is often at one place on the circumference of the coin either a blank in the milling or file marks in place of the cast milling It is assumed that this is the place where the "tail" has been removed, and that it represents the point on the circumference where the metal entered the mould. It has been noted that the position of the orifice in the mould (as indicated on the milling) in relation to the inscription is often the same on several coins. This may, perhaps, point to a common origin.

QUESTIONED DOCUMENTS.—During 1930, documents have frequently been submitted with a request for an opinion as to the age of the writing, but, generally speaking, conditions have been unfavourable to any useful opinion being given. In one case in which two documents were alleged to have been written at the same time, it was possible to produce evidence to the contrary.

A bundle of burnt currency notes was submitted for identification. By careful treatment in a fluid medium, it was possible to effect the separation of some of the notes and to decipher parts of the inscriptions, and, in some instances, the numbers.

The examination of a rubber stamp impression on a forged passport has suggested that in this connection the detection of forgery would be greatly facilitated if every rubber stamp in use by the Government could be distinguished by a number or other mark.

HOT SPRINGS OF PALESTINE.—The hot springs at Tiberias and El Hamme are of interest. The El Hamme waters are potable and contain up to 0·7 parts of hydrogen sulphide per 100,000. The Tiberias springs are strongly saline and contain only traces of hydrogen sulphide.

The following results (parts per 100,000) were obtained:

	Tiberias main spring.	El Hamme main spring.
Chlorides (calculated as chlorine)..	1930	40
Total solids (dried at 140° C.) ..	3220	110
Hydrogen sulphide	0·07	0·75
Temperature at spring head ..	60° C.	47° C.

Federated Malay States

ANNUAL REPORT OF THE CHIEF CHEMIST FOR THE YEAR 1930

THE chemical work for various Departments of the Federated Malay States is carried out by the Institute for Medical Research, whose Chief Chemist is Mr. R. W. Blair, F.I.C. The work for the Medical Department includes the analysis of water, milk, sewage effluents and toddy, and biochemical and toxicological examinations.

MILK.—The Sale of Food and Drugs Enactment, 1913, prescribes standards of 3·25 per cent. of fat and 8·5 per cent. of solids-not-fat. Of the 840 samples taken by the officers of the Health Branch, 13 were deficient in fat and 54 in solids-not-fat.

SEWAGE EFFLUENTS.—Most of the 93 samples examined failed to conform to the standards prescribed by the Royal Commission on sewage disposal.

DELETERIOUS DRUGS.—Eight substances supposed to contain drugs specified in the Deleterious Drugs Enactment were examined for the Police Department, and in two of them the leaves and seeds of Indian hemp (*Cannabis indica*), known also as "ganja," were identified.

Coins and Coining Material.—Of the 2011 exhibits in counterfeit coining cases, 1533 were counterfeit coins. Other exhibits included 11 moulds and 5 powders (plaster of Paris).

Extract of Rice Polishings.—In addition to 9504 fluid ounces of the former liquid preparation, manufacture on an extended scale of the powder (acid clay) extract was commenced, and 110 kilos. were prepared.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Determination of Starch in Cereal Products, with Special Reference to Rice. E. H. Hall. (*J. Soc. Chem. Ind.*, 1931, **50**, 429T–434T.)—In this contribution to the vexed question of starch determination, the author points out that confusion has arisen owing to attempts to force a naturally occurring substance like starch into an analytical mould and to define starch arbitrarily in terms of somewhat doubtful chemical entities, such as hemicelluloses, amylopectins, and amyloses. From the starch manufacturer's standpoint, starch means all that is included in and within the envelope of the starch granule, and nothing more, the reactions towards different enzymes or dispersing agents, or the names given to the constituents, being immaterial.

Results of determinations by Ling's barley-diastase method, Davis and Daish's taka-diastase method, and the like, where it is definitely known that part of the starch granule is not included, should be returned as "amylose," as distinguished from starch. Rask's method, described by Herd and Kent-Jones (Analyst, 1931, **56**, 184), would appear, from its very nature, to be subject to various sources of error, such as the absorption of starch from its highly colloidal hydrochloric acid dispersion by fibre, protein, etc., which are filtered off, the danger of enclosing globules of unattacked starch, and the risk of not precipitating with alcohol all that was dispersed colloidally by the acid. The view is expressed that Rask's method cannot serve as a check on the results given by other methods.

In the light of these considerations, it is shown that starch may be easily, accurately, and comparatively quickly, determined, in the case of rice, by a combination of O'Sullivan's and Brown's methods, or by a suitable modification of Brown's method alone; this modification is probably applicable also to other cereals. The procedure recommended is as follows: 2·2 grms. of rice (ground and sieved through an 80-mesh sieve) are extracted in a Soxhlet extractor with alcohol (sp. gr. 0·92) for 1 hour, the extracted rice being then transferred to a tall 250 c.c. beaker, fitted with a cover-glass, cut to accommodate a stirring rod. The volume is made up to about 70 c.c. with distilled water, and the whole is heated to boiling, and kept boiling for 2 minutes, being well stirred meanwhile to prevent bumping and frothing. The rod is left in the beaker and the cover replaced (to prevent the starch gel from skinning over), the temperature being allowed to fall to 60° C. Five c.c. of malt extract are now added; this is made by extracting ground malt of suitable diastatic power (at least 40 to 50 Lintner) with 20 times its weight of distilled water, and filtering till crystal-bright. The contents of the beaker are now well stirred, left for 3 minutes, heated to boiling, and kept boiling for 1½ minutes, cooled somewhat and transferred to a 100 c.c. sugar flask, the volume being kept below 100 c.c. Two c.c. of a buffer solution, made by mixing 500 c.c. of *N* sodium acetate solution with 5 c.c. of glacial acetic acid, are next added; this gives the *p*H value 5·4 after addition of the malt extract. The stopper is placed loosely in the flask, which is immersed for 15 minutes in a bath maintained as nearly as possible at 57° C. The volume is made up to 100 c.c., 10 c.c. of the malt extract are added, the stopper is replaced, and the flask is left in the bath for 60 minutes. It is then withdrawn and, the stopper having been tested for looseness, heated in a boiling water-bath for 20 minutes, and afterwards placed in a cooling bath. The contents are washed into a 250-c.c. measuring flask, made up to volume, and filtered through a fluted filter large enough to receive the whole at once (Whatman No. 12 of 24 cm. diameter is suitable); filtration is very rapid. The perfectly bright filtrate is titrated against 25 c.c. of Fehling's solution according to the directions of Lane and Eynon (ANALYST, 1923, **48**, 220) (the author reads "anhydrous maltose" for "hydrated maltose" in Lane and Eynon's Table V). After deduction of a "blank" value corresponding with 15 c.c. of malt extract, the maltose found is divided by the maltose-starch factor, to convert it into starch. With rice starch, when a malt having the diastatic power 46 Lintner is used, this factor may be taken as 0·824, which agrees with Brown's figures for malt, but it may be determined readily by a determination on the carefully purified starch in question. Three determinations by this method can be made comfortably in a day by one worker. The malt extract must be used within 24 hours of its preparation; it should be kept in a stoppered flask in presence of a few drops of toluene, and the blank should be re-determined every time it is used. As the same maltose-starch factor holds for rice as for barley and malt, it is most probable that Brown's method, especially when modified as above, is of very general application.

T. H. P.

Chemical Composition of Shea Fat. S. J. Hopkins and F. G. Young. (*J. Soc. Chem. Ind.*, 1931, **50**, 389T.)—Two specimens of shea butter have been examined, one consisting of crude and the other of refined fat. The authors show that the analytical data for these fall within the usually accepted limits, and they have also examined the fatty acids and non-saponifiable fraction. Inferences are drawn regarding the composition of the fatty acids, and a hydrocarbon, apparently identical with illipene, was isolated in considerable quantities from the non-saponifiable fraction.

Composition of Cherry Gum. C. L. Butler and L. H. Cretcher. (*J. Amer. Chem. Soc.*, 1931, **53**, 4160–4167.)—The air-dried gum, which was collected at Montezuma, Indiana, from wild cherry trees, contained 10·75 per cent. of water and 1·5 of ash. Only 14·5 per cent. was soluble in water, and the methoxyl test by the Zeisel method gave a negative result. The approximate composition of the dry gum was:—Ash, 1·3; galactose, 27·7; total pentose, 56·1; arabinose (diphenylhydrazone method), 31·6; other pentose (calculated as xylose), 24·5; and uronic acid, 10·1 per cent.; methyl pentose and mannose absent. By hydrolysis of the gum in 0·5 *N* sulphuric acid at 90° C. for 5 hours all the pentose and practically all the galactose were split from the acidic nucleus, and the acidic fraction (isolated as barium salt) had barium and aldehyde contents of a salt of an acid consisting of 2 uronic groups and 3 hexose sugar residues corresponding with mannose. Further hydrolysis of the acid of the barium salt gave another acidic fraction, which was isolated as barium salt and hydrolysed still further, and it was eventually established that the uronic acid present was glucuronic acid. The degradation products of the cherry gum, obtained by hydrolysis in acid solution, are arabinose, xylose, galactose, mannose and glucoronic acid. D. G. H.

Rapid Method for Determining Acid-Soluble Phosphoric Acid in Eggs. J. Fitelson and I. A. Gaines. (*J. Assoc. Off. Agric. Chem.*, 1931, **14**, 558–562.)—The following procedure is more rapid than, and gives results comparable with those of, Pine's method for the determination in eggs of the acid-soluble phosphoric acid (ANALYST, 1924, **49**, 531), which Pine regarded as a better index of decomposition in eggs than the ratio between inorganic and total phosphorus studied by Chapin and Powick (*J. Biol. Chem.*, 1915, **20**, 97); it is applicable more especially to dried egg-yolk.

Twelve grms. of the dried yolk (25 grms. of dried whole egg, 50 grms. of liquid whole egg, or 25 grms. of liquid yolk) are treated in an 8 oz.-centrifuge bottle with exactly 150 c.c. of freshly-made saturated picric acid solution (treated immediately before use with 0·75 c.c. of concentrated hydrochloric acid) and a pinch of solid picric acid to ensure saturation. The bottle is stoppered, shaken vigorously by hand for a few minutes, and then in a machine for 30 minutes. The whole is centrifuged and filtered through a folded filter paper (the egg material should not remain in contact with the acid solution for more than 1¾ hours, including the time required for filtration). Of the filtrate, 100 c.c. are boiled in a 300-c.c. Kjeldahl flask with 5 c.c. of concentrated sulphuric acid, 20 c.c. of concentrated nitric acid and a few glass beads, until white fumes appear. Nitric acid is added in small quantities until a practically colourless solution is obtained when the white fumes appear, the boiling being then continued for 30 minutes. The liquid is cooled, washed into a 400-c.c. beaker (the total volume being kept below 100 c.c.), treated with 10 grms. of ammonium nitrate, made alkaline to litmus with strong ammonia solution, and slightly acidified with nitric acid. After being cooled to 25 to 30° C., the liquid is stirred mechanically for at least 30 minutes with 45 c.c. of ammonium molybdate precipitant [*Methods of Analysis, A.O.A.C.*, 1925, 3, 8(*a*)]. The determination is completed in the usual manner [*ibid.*, 3, 10(*a*)]. A correction is applied to the volume of the extraction solution for the water in the egg, and the result is returned as mgrms. of P_2O_5 per 100 grms. of dry egg. T. H. P.

Detection of Added Lecithin in Chocolate Products. W. O. Winkler and J. W. Sale. (*J. Assoc. Off. Agric. Chem.*, 1931, **14**, 537–547.)—Six methods of determining lecithin in cacao products have been tried, the best results being obtained by a modification of the tentative method given in *Methods of Analysis of the Assoc. Off. Agric. Chem.* (2nd Edition, 1925, 322), petroleum spirit and alcohol being used for the extraction.

The lecithin content of 27 samples of raw and roasted cacao beans and liquors, representing 10 varieties of beans, was found to range from 0·47 to 0·88 per cent., calculated on the fat. According to manufacturers of chocolate and distributors of lecithin, the proper amount of lecithin to add to sweet coatings is about 0·3 per cent., which is equivalent to about 1 per cent. on the fat; such a proportion can be readily detected and fairly accurately determined by the method used. No material change in the lecithin content was noted when cacao beans were roasted at temperatures and for periods of time corresponding with commercial practice.

T. H. P.

Detection of Peroxides in Ether. L. W. Green and R. E. Schoetzow. (*Amer. J. Pharm.*, 1931, **103**, 603–605.)—The chromic acid test for the detection of peroxides developed in ethers (Leffmann and Pines, ANALYST, 1930, **55**, 399) was not found to be as sensitive as the U.S.P., *X*. test, and the presence of aldehyde still further diminished its sensitivity. By using 10 c.c. of ether and shaking thoroughly, instead of pouring the reagent through the ether, the sensitivity of the chromic acid test was increased, but could not be made to equal that of the U.S.P. test. In applying that test it is desirable to avoid vigorous shaking, to observe the appearance from time to time, instead of only at the end of an hour, and to examine the contents of the cylinder vertically as well as horizontally, since the free iodine tends to leave the aqueous layer and to be dissipated in the ether on further shaking.

D. G. H.

Determination of Strychnine in Easton's Syrup. L. A. Haddock and N. Evers. (*Quart. J. Pharm.*, 1931, 4, 314–319.)—The individual stages of Evers's method (*Yearbook Pharm.*, 1922, 409) have been examined, and the method is modified as follows:—The total alkaloids are dissolved and transferred to a separator by means of 20 c.c. and 5 c.c. portions of *N* hydrochloric acid, 25 c.c. of saturated sodium chloride solution being used for washings. This mixture is shaken for 5 minutes each time with five 25-c.c. portions of chloroform, and the combined extracts are shaken for 5 minutes with two 5-c.c. portions of a mixture of equal volumes of *N* hydrochloric acid and saturated sodium chloride solution. These washings are then shaken with 10 c.c. of chloroform, and the combined chloroform extracts are shaken, first with a mixture of 20 c.c. of water and 5 c.c. of 10 per cent. ammonia, and then with 5 c.c. of water. The chloroform solution is separated, evaporated, and, after the addition of 1 c.c. of alcohol, re-evaporated, the residue being dried at 100° C., and washed by decantation through cotton-wool with three 2 c.c. portions of a mixture (2:1) of ether and petroleum spirit saturated with strychnine. Any alkaloids on the wool are washed back into the flask with 3 c.c. of chloroform, 1 c.c. of alcohol is added, the solution is evaporated, and the strychnine is dried at 100° C. until constant in weight. If the syrup is used, 50 c.c. are taken with 50 c.c. of saturated salt solution and 5 c.c. of concentrated hydrochloric acid, and the quantities are doubled throughout. This method avoids the incomplete extraction of strychnine, which was probably balanced in the earlier method by the presence of quinine in the residue. The maximum recorded error for 0·01 to 0·05 grm. of strychnine in the presence of 1·5 grm. of quinine is ±5 mgrms. J. G.

Biological and Spectroscopic Tests on Ergot Alkaloids, with Notes on the Maurice Smith Colour Test. F. Wokes and H. Crocker. (*Quart. J. Pharm.*, 1931, 4, 420–443.)—The spectroscopic work was carried out with a Hilger photographic quartz (ultra-violet) spectroscope with an iron-nickel or water-immersed tungsten arc, the extinction coefficient being found by means of a Hilger-Nutting spectrophotometer; its average deviation from the mean of at least 5 readings was not greater than 0·03. Readings were taken every 3 or 10$\mu\mu$ over the whole absorption range (200 to 700$\mu\mu$) for 0·02 per cent. solutions of the alkaloids in 1 per cent. tartaric acid or in alcohol, and for the blue colour obtained in Smith's test (*U.S. Public Health Repts.*, 1930, **45**, 1466), the results being compared against biological standardisation by Clark and Broom's method (ANALYST, 1923, **48**, 498). In the Smith test 2 c.c. of the acid solution of alkaloid are layered on 2 c.c. of a 2·5 per cent. solution of *p*-dimethyl-amino-benzaldehyde in concentrated sulphuric acid, and 2 c.c. of water are then added. The layers are mixed, with the tube immersed in cold water, and the mixture is exposed for 2 hours at a distance of 15 cm. from a mercury vapour lamp, with a water-filter to eliminate heat rays, the reaction being complete when the blue colour, as evaluated in the tintometer, has ceased to increase. This test frequently gave results higher than those from the biological method; *e.g.* it indicated that ergotinine and ergotaminine are almost equal in activity to ergotoxine, though, biologically, their activities are only about one-tenth. Ergotamine has an activity by the biological method 0·8 to 0·9 that of ergotoxine. Solutions of ergotoxine, ergotamine, ergotinine and ergotaminine are all unstable and in concentrations of 0·001 per cent. all show a characteristic absorption band with a maximum at about 316$\mu\mu$, due, probably, to a common molecular grouping. Ergotinine and ergotaminine also give a secondary band (maximum at 242 $\mu\mu$), which, however, is unsuitable for quantitative differentiation of these from ergotoxine and ergotamine. Smith's reaction gave a principal band at 580$\mu\mu$, and a secondary band at 401$\mu\mu$, but neither the tintometric nor the spectrophotometric method for the measurement of colour intensity indicated that this test provides a satisfactory method of estimating physiological activity; the origin of the blue colour is not necessarily that of the 316$\mu\mu$ band. It is concluded that the spectroscope gives high results, and cannot replace the biological method for the estimation of the activity of fresh or deteriorated preparations of these alkaloids, fair agreement being obtained only with fresh and deteriorated ergotoxine ethane sulphonate. J. G.

Assay of Official Balsams. T. T. Cocking. (*Quart. J. Pharm.*, 1931, 4, 330–334.)—Total balsamic acids are determined by saponification of 2·5 grms. of prepared storax or tolu balsam, or of the alcoholic extract from 2·5 grms. of benzoin, by 25 c.c. of boiling 0·5 *N* alcoholic potassium hydroxide solution in the usual way. The potassium salts of the balsamic and resin acids, potassium hydroxide, and aromatic and resinoid alcohols, which remain after evaporation of the alcohol, are digested with 50 c.c. of hot water, 150 c.c. of cold water being then added to the cooled mixture, and the resin acids precipitated by the addition of 50 c.c. of a 5 per cent. solution of crystalline magnesium sulphate. The precipitate (salts of resin acids and magnesium hydroxide) is removed by filtration on a Buchner funnel and washed with a little water, the alkaline filtrate (magnesium salts of balsamic acids, aromatic alcohols, etc.) is acidified with hydrochloric acid, and the balsamic acids are extracted in ether. In order to ensure complete separation of the acids from the alkali-soluble aromatic alcohols, the ethereal solution is extracted 5 times with a 5 per cent. solution of sodium hydrogen carbonate, each separated portion being washed with a little ether. The total alkaline solutions are then acidified with hydrochloric acid and extracted with ether, and the residue is weighed after evaporation and vacuum-desiccation over sulphuric acid. Tolu and benzoin give mixtures of benzoic and cinnamic acids, but storax gives the latter only (99 per cent. purity) which may be titrated. In the case of tolu (and benzoin) difficulty may be experienced in the neutralisation of the free acids, and in the production of a uniform suspension containing their potassium salts. The balsam (2·5 grms.) is, therefore, dissolved in 15 c.c. of hot 90 per cent. alcohol, and 10 c.c. of potassium hydroxide solution (B.P.) and 50 c.c. of water are added at once, the resulting brown translucent mixture being immediately diluted with 150 c.c. of water. The magnesium sulphate solution may then be added, and after 5 minutes on the water-bath to coagulate the precipitated salts and magnesium hydroxide, the mixture is cooled and filtered, and the total balsamic acids are separated from the filtrate as described. It is suggested that these methods are preferable to, and should replace, that previously suggested (Hill and Cocking, *Chem. and Druggist*, 1912, **80**, 412, 789) for inclusion in the B.P. J. G.

Determination of Phenolphthalein in the Presence of Caffeine and Cinchona Alkaloids and Drugs containing Anthraquinone. (*Amer. J Pharm.*, 1931, **103**, 609–610.)—To 25 c.c. of water in a separating funnel is added 1 c.c. of the medicine under investigation, followed by 1 c.c. of concentrated hydrochloric acid. Three extractions, each with 50 c.c. of ether, are made, and the extracts are washed with 25 c.c. of water. The water is discarded, and the ether is evaporated in a current of air from a 400-c.c. beaker. The residue is taken up with 5 c.c. of 95 per cent. alcohol, transferred to a 100-c.c. cylinder, the beaker is washed with 25 c.c. of water and 5 c.c. of 10 per cent. ammonia, and the whole is made up to 100 c.c. and mixed. A standard containing ¼ grain of phenolphthalein per fluid oz. is made up similarly, 1 c.c. of the standard in 100 c.c. being taken for comparison. One cylinder contains 1/120th of a grain of phenolphthalein and the other an unknown quantity from the medicine. If the sample shows an appreciably darker colour than the standard, 50 c.c. (or 25 c.c.) are diluted to 100 c.c., to get a sample somewhat approximating the colour to read in the colorimeter tubes; or, if necessary, the standard is diluted. The depth of colour is then found in Schreiner tubes, graduated in mm., and the quantity of phenolphthalein is calculated. Emodin-bearing drugs, in amounts up to 15 grains per fluid oz., do not affect the analysis. D. G. H.

Syrup of Senna and the Dispensing of Syrups in Wet Bottles. T. McLachlan. (*Quart. J. Pharm.*, 1931, **4**, 461–464.)—(1) Analyses are given of seven commercial samples:—Sp. gr. (15/15° C.), 1·2278 to 1·3082; total solids, 49·8 to 68·0 per cent.; sucrose, 36·1 to 54·4 (in one case 0·4) per cent.; invert sugar, 2·1 to 9·8 (in one case, the same as above, 44·2) per cent.; senna extract, 4·0 to 14·4 per cent. The exceptional sample was probably not made from cane sugar, since the *p*H was only 4·5, and cane sugar would not be completely inverted at ordinary temperatures at this acidity, even on prolonged keeping. The present Pharmacopoeia rulings are not sufficiently rigid as regards manufacture and standardisation of the syrup, especially since the purgative action may be destroyed if the extract is heated. (2) Syrups dispensed in rinsed bottles, which have been carelessly drained, may contain 0·3 to 4·6 or 0·4 to 6·5 per cent. of added water, according to whether the bottles are still or rotated while draining, respectively. This water may prove of importance when the sugar content of a preparation is adjusted so as to prevent either crystallisation or fermentation, and 2 per cent. of added water is considered the maximum safe addition. J. G.

Procaine Borate. G. W. Collins. (*Amer. J. Pharm.*, 1931, **103**, 555–559.)—The Council on Pharmacy and Chemistry (U.S.A.) have adopted the following standards for procaine borate for inclusion in "New and Non-Official Remedies":—Formula: $C_6H_4.NH_2COO.C_2H_4.N(C_2H_5)_2 5HBO_2$; a borate formed by the interaction of *p*-aminobenzoyl-diethylamino-ethanol and boric acid in the same organic solvent. Procaine borate, which closely resembles procaine hydrochloride in action and can be used for the same purposes, occurs as a fine, white odourless crystalline powder, soluble in water, soluble in alcohol (about 1 : 4); insoluble in acetone, benzene, chloroform and ether. Its aqueous solution (1 in 10) is alkaline to litmus, dissociates hydrolytically, and "melts" at 163° to 166° C. After adding 25 c.c. of water to 1 grm. of the procaine borate in a separating funnel, followed by 5 c.c. of *N* sodium hydroxide solution, and extracting with 25 c.c., 20 c.c. and 10 c.c. of chloroform, successively, the oily semi-solid residue from the chloroform extract is dissolved in 25 c.c. of a 2 per cent. solution of hydrochloric acid. Portions of this solution should respond to the tests for procaine hydrochloride. On dissolving 0·1 grm. of procaine borate in 2 c.c. of methyl alcohol, adding 5 drops of sulphuric acid, and igniting, the flame shows a green outer zone. Ten c.c. portions of a solution of 0·5 grm. in 50 c.c. of water should yield no opalescence with 1 c.c. of dilute nitric acid, and 1 c.c. of silver nitrate solution; no turbidity with 1 c.c. of diluted hydrochloric acid and 1 c.c. of barium chloride solution, and no coloration or precipitate on saturation with hydrogen sulphide. The substance should pass the arsenic test, and the limit of uncombined *p*-aminobenzoyl-diethylamino-ethanol should be 2 per cent. This is determined by adding 25 c.c. of chloroform to 0·5 grm. of the borate, shaking for 5 minutes, and, after standing, filtering the liquid, washing the insoluble portion on to a filter, adding the washings to the extract, evaporating the chloroform, and drying and weighing the residue. The amount of *p*-aminobenzoyl-diethylamino-ethanol, calculated on the dried substance, should be between 50 and 52 per cent., and that of *m*-boric acid (HBO_2) between 47 and 48·5 per cent., as determined by the Gladding method of distillation and subsequent titration. D. G. H.

Corrosion of Tin Plate. Pellerin and Lasausse. (*Chimie et Ind.*, **1931**, **204**; *Food Manufacture*, **1931, 6, 328–329.**)—Acetic and citric acids were used alone in this investigation, in the presence and absence of air, and in the presence and absence of common salt and phosphates. The tests were made in tin plate containers, heated in an autoclave at 112° to 115° C. It was found that oxygen favours attack by citric acid, specially at the level of the liquid. Boiled and unboiled solutions of citric acid, and also of acid and salt, were used in lacquered and unlacquered tins, and the experiments again indicated that oxygen favours the attack of tin plate by citric acid, and that salt retards solution of tin and activates that of iron, the lacquer tending to induce solution of both iron and tin. Comparative tests with acetic acid showed the same effect of oxygen, but acetic acid attacks the iron rather than the tin. The effect of the *p*H of the acid solutions on the corrosion of tin plate was studied by adding disodium phosphate to the acid solutions to give a range of *p*H 5 to 7·7. After sterilisation, the acetic solution of *p*H 6·7 to 7·7, was free from tin and iron and the metal was bright; at *p*H 5·0 there were traces of iron in the solution, and the metal was rusty in places in the unfilled area. Acetic acid, used alone, produced corrosion; citric acid by itself caused tin and iron to dissolve, the quantity of tin increasing as the *p*H rose from 5 to 7·7, and the iron increasing with change of *p*H from 7·0 to 5·0, no iron being present when the *p*H was 7·7. Acetic acid (15 grms. per litre) caused, in 5 months, blowing of all containers, which had been kept at 38° C. after sterilisation in the presence of either air or salt, and iron, but no tin was found in solution. With citric acid, about half the number of tins were "blown" under the same conditions, and all the solutions contained tin, but only traces of iron. Acetic acid, even at low concentrations, attacks iron so readily that "blowing" ensues; but, although citric acid dissolves tin, no "blowing" occurs at low concentration. Fatty acids can attack tin plate. *Pâté de fois gras* was tinned and examined for tin and iron after (*a*) 10 and (*b*) 20 months. The amounts of metal dissolved from cans with single tinning were: Tin (in mgrms. per kilo.): (*a*), 137, (*b*), 344; iron, (*a*), 54, (*b*) 68; with double tinning: Tin, (*a*), 110; (*b*), 467; iron, (*a*), 55; (*b*), 85; from lacquered cans: Tin, (*a*) 100, (*b*) 105; iron, (*a*) 55, (*b*) 152. The lacquer film probably limits the attack on tin to the small surfaces exposed by cracking of the lacquer in manufacture. A pork meat paste acted similarly. Acetic acid corrosion was typified by that produced by pickled fish, and results obtained with preserved mushrooms were similar to those for citric acid alone. A neutral product, green peas, after 18 months' storage, showed for (*a*) tin, and (*b*) iron: with single tinning, (*a*) 72 mgrms. per kilo., (*b*) 71; with double tinning, (*a*) 38, (*b*) 33; and with lacquered cans, (*a*) 23, (*b*) 48. The retarding effect of sodium phosphate on corrosion is attributed to the formation of a thin film of insoluble phosphate over the metal surface. D. G. H.

Biochemical

Effect of Diet on Manganese Content of Milk. A. R. Kemmerer and W. R. Todd. (*J. Biol. Chem.*, 1931, **94**, 317–321.)—Within the past year several workers have used milk as a manganese-low diet for studies on the rôle of this element in animal metabolism. Cow's milk is being used so extensively in these experiments that the question of the variation in the manganese content of milk becomes an important one. If the manganese content of milk is easily affected by the amount of this element in the ration, care must be used in choosing the milk for the work. Experiments are described on the manganese content of milk from cows and goats, when given a standard ration and when given the same ration plus manganese. The results show that milk produced by cows on a normal ration contains approximately 0·03 mgrm. of manganese per litre. The manganese content of cow's milk was not increased when sufficient manganous sulphate was added to the ration to increase the manganese intake five-fold. However, the amount in the milk used cannot be ignored, because the amount may vary with the other factors, such as the individual, the breed, and the period of lactation. The manganese content of milk from goats on a normal ration is approximately 0·082 mgrm. per litre, more than twice the amount present in cow's milk. This fact is rather significant, since no such differences were observed between cow's milk and goat's milk in the case of iron and copper. The addition of manganous sulphate, in quantities sufficient to increase the manganese intake five to tenfold, increased the manganese content of goat's milk very slightly. The increase was especially noticeable during the 4th and 5th weeks on the supplemented ration. This difference may be partly due to the decrease in the milk production, because there was a definite decrease in the amount of milk produced during the latter part of the experiment. P. H. P.

Composition of Vixen Milk. E. G. Young and G. A. Grant. (*J. Biol. Chem.*, 1931, 93, 805–810.)—Fox farming is practised extensively in certain sections of Eastern Canada, notably Prince Edward Island. Occasionally the problem arises of rearing by artificial means a litter of fox puppies deprived of their mother. The most successful way is to introduce them into a litter of kittens, from which they are almost indistinguishable. If the mother cat accepts them the growth is usually good. On artificial feeding by cow's milk the mortality is high. No analysis of the milk of the fox could be found in the literature, and it was considered of sufficient importance commercially to make one. The milk can only be obtained in the spring and, of course, from an animal that is relatively tame. A sample of milk obtained from a well-furred medium silver fox, after about 4 weeks of lactation, was of a slightly yellowish colour, of a thick, creamy consistence, and of a faint, asphalt-like odour; it settled into 3 distinct layers. The average composition of the milk of five vixens was as follows:—Water, 81·87; total solids, 18·13; proteins, 6·25; fat, 6·30; lactose, 4·56; and ash, 0·96 per cent. Calcium and phosphate comprise about 74 per cent. of the ash, but the variation is wide. With one sample a figure of 86 per cent. was obtained. A sample of colostrum was also analysed. A table shows analyses of milk of other animals. Compared with the milk of the fox, the milk of the cat is slightly lower in protein, intermediate in fat, and similar in lactose and salt content. Compared with the milk of the cow, that of the fox is distinctly different and richer in protein, fat, and calcium phosphate. It is not surprising, on this basis alone, that the fox puppy does not thrive on cow's milk. The milk of the ewe probably shows the greatest similarity. P. H. P.

Interferometric Determination of Alcohol in Blood. J. C. Bock. (*J. Biol. Chem.*, 1931, 93, 645–655.)—A rapid and accurate method for the determination of alcohol in normal blood is presented. It has been found that the alcohol in the blood of adults, taken before breakfast, about 12 hours after the last meal, fluctuates from 0·0015 per cent. to 0·0113 per cent., the majority of cases varying only from 0·003 to 0·005 per cent. of ethyl alcohol. The method consists in the removal of the blood proteins with a single reagent, distillation in a very simple distilling apparatus, and determination of the alcohol by means of an interferometer. Kionka (*Pharmakologische Beiträge zur Alkoholfrage*, Jena, 1927, pt. 1) used this instrument for the same purpose, but he distilled the alcohol from the whole blood *in vacuo*, and used a very complicated, costly and fragile apparatus. The Löwe-Zeiss interferometer for liquids (and gases) is an instrument which measures the *difference* of the refractive indices of two liquids or solutions; it is capable of measuring refraction differences of liquids within 2 units of the seventh decimal. The method of making interferometric measurements and the distillation apparatus devised are carefully described. The condenser tube is made of silver or copper tubing, and precautions for washing it are given. For the removal of proteins from the blood, a phosphomolybdic acid reagent was found satisfactory. It gives a coarse precipitate and ample filtrate. The composition is as follows: 12 grms. of phosphomolybdic acid and 10 grms. of sodium sulphate (crystals) are dissolved in about 600 ml. of water; 9 ml. of concentrated sulphuric acid are added, and then the solution is boiled for approximately 15 minutes. It is cooled and made up to 1 litre. For the procedure 10 ml. of blood are run slowly into a 50 ml. glass-stoppered volumetric flask, containing about 35 ml. of the phosphomolybdic acid reagent. The flask is gently agitated (not shaken), and filled to the mark with reagent. The contents are mixed, left for 10 minutes, and transferred to a 50 ml. centrifuge tube. This tube has a slightly constricted neck, and is closed with a rubber cap. It is centrifuged for about 10 minutes at high speed. The supernatant liquid is poured through a small coarse filter; 25 ml. of filtrate are transferred to the distilling flask and distilled at a moderate rate until about 20 ml. have been received in a 25 ml. volumetric flask. The contents are made up to volume, mixed, and the alcohol is determined in the interferometer. Tests were made for losses of alcohol in manipulation by comparisons of alcohol solutions of different concentrations, which had been centrifuged, filtered and distilled with those that had not. The greatest variation from the theoretical reading, the zero value, was 4 scale divisions, but 93 per cent. of the results showed readings within ±1 of the zero value, 2 scale divisions being equivalent to 0·001 per cent. of ethanol when an 80 mm. chamber was used. Alcohol added to blood was recovered with very small errors, varying from +0·0005 to −0·0015 per cent. P. H. P.

Gasometric Method for the Determination of Lactic Acid in the Blood. B. F. Avery and A. B. Hastings. (*J. Biol. Chem.*, 1931, 94, 273–280.)—A new method is described for the determination of lactic acid in the blood. Whole blood or serum is first treated by the tungstic acid method of Folin and Wu for the removal of protein. The filtrate is then treated with 14 per cent. copper sulphate solution and 14 per cent. calcium hydroxide suspension for the removal of sugar and other interfering substances. The lactic acid in the filtrate is oxidised to carbon dioxide by potassium permanganate in the Van Slyke manometric gas apparatus (*J. Biol. Chem.*, 1927, **73**, 121), 1 molecule of lactic acid yielding 1 molecule of carbon dioxide. A table shows the results of the gasometric determination of lactic acid in lithium lactate solutions of various concentrations. Reasonably accurate determinations can be made on samples of lactic acid varying in amount from 0·045 to 0·720 mgrm. Known amounts of lithium lactate were added to blood serum, which was then subjected to the tungstic acid and to the copper sulphate and calcium hydroxide treatment. The results were within 2 per cent. of the theoretical amounts. Parallel determinations by the gasometric method and by the Friedemann and Kendall (*J. Biol. Chem.*, 1929, **82**, 23) modification of the distillation method of Friedemann, Cotonio and Shaffer (*J. Biol. Chem.*, 1927, **73**, 335; ANALYST, 1927, **52**, 418) were made on (1) standard lithium lactate solutions, (2) whole blood, (3) serum, and (4) serum to which varying amounts of lithium lactate had been added. Both methods gave essentially the same results on pure lithium lactate solutions, but the gasometric method figures on whole blood or serum were from 0·38 to 0·71μ per litre higher than those by the distillation method. The difference between the two methods is relatively constant for varying lactate concentrations, and, therefore, it is proposed that 0·5μ per litre should be subtracted from results obtained gasometrically for blood lactate concentrations. Lactate concentrations obtained in this way should be consistent with those obtained by the Friedemann, Cotonio and Shaffer method. The advantages of the gasometric method over others are the small amount of material required, the speed and simplicity of determination, and the lack of need for special apparatus other than the Van Slyke manometric gas apparatus. Its disadvantage lies in the fact that an empirical correction must be applied if results comparable with those obtained by the distillation method are desired. P. H. P.

Determination of Glycogen in Tissues. M. Sahyun. (*J. Biol. Chem.*, 1931, **93**, 227–234.)—The method of Pflüger (*Arch. ges. Physiol.*, 1904, **103**, 169) for the determination of glycogen has been modified and made available for small amounts of tissue. The suggested modifications involve (*a*) shortening of the time necessary to hydrolyse the tissue with strong alkali (30 to 40 minutes is now recommended), (*b*) facilitation of the separation of the glycogen by precipitating it in the presence of charcoal and centrifuging, (*c*) hydrolysis of the separated glycogen for a shorter time than customary (for only 2 hours with 1 *N* sulphuric acid), and (*d*) the substitution of sulphuric acid for hydrochloric acid to avoid the introduction of chlorides. For the method, 1 grm. or less of tissues, frozen in liquid air, is introduced into a 15 c.c. graduated centrifuge tube, and enough 40 per cent. potassium hydroxide is added to bring the mixture to the 5 c.c. mark. If larger amounts of tissues are obtainable, to each grm. of the tissues used in a 50 c.c. centrifuge tube, 1 c.c. of 60 per cent. potassium hydroxide solution is added, so that the final volume of the alkali mixture does not exceed 10 or 15 c.c. The tubes are covered with tinfoil, placed in a boiling water-bath for 30 or 40 minutes, and shaken thoroughly every 5 or 10 minutes. About 50 mgrms. of active charcoal are then added, and the contents are well stirred with a fine glass rod, after which twice the volume of ethyl alcohol is added to the alkali mixture, and the contents are again stirred. Any glycogen sticking to the rod is washed with as small an amount of hot water as possible into the tube, and twice that volume of alcohol is added. The tubes are centrifuged for 10 minutes. The glycogen is adsorbed completely on the charcoal and collects at the bottom of the centrifuge tube. The alkali-alcohol supernatant liquid is discarded. Five c.c. of hot distilled water, or less, are added, and a strip of litmus paper. A few drops of 2 *N* sulphuric acid are added to turn the blue litmus paper red, and this is followed by an equal volume of acid of this concentration. The centrifuge tubes are then replaced for 2 hours in the boiling water-bath, whereupon hydrolysis is complete. The contents are neutralised with 1 *N* or 2 *N* sodium hydroxide and introduced quantitatively into volumetric flasks. The mixture is cooled, diluted to the mark, and mixed thoroughly, and samples are removed and filtered. The filtrate is clear and colourless, and ready for sugar determinations. The reducing sugar is determined by the method of Folin and Wu (*J. Biol. Chem.*, 1920, **41**, 367), and the corresponding values in terms of glycogen are obtained by multiplying the value obtained for glucose by the factor 0·927. A table shows very good results obtained for the recovery of glycogen, added to glycogen-free tissues. An experiment which shows the effect of the presence of chloride on the Folin and Wu sugar method is described. The influence of sodium sulphate (1 *N* to 0·01 *N*) on sugar determinations was investigated; no change was observed in the final blue colour for 40 minutes, except in solutions containing 1 *N* sodium sulphate. In concentrations of 0·6 *N* sodium sulphate there was a stabilisation of the final blue colour. It was, therefore, found convenient to prepare the alkaline copper reagent of Folin and Wu in 0·6 *N* sodium sulphate solution. P. H. P.

Action of Trypsin on Different Types of Wool. C. Fromageot and A. Porcherel. (*Compt. rend.*, 1931, **193**, 788.)—Samples of three types of wool, each weighing 300 mgrms., were treated for 48 hours at 37° C. with a sodium borate and soda buffer solution at *p*H=11. After being washed, they were placed in 50 c.c. of a 1 per cent. trypsin solution at 37° C. and brought to *p*H=8 by the use of a sodium borate and hydrochloric acid buffer solution. There was a steady loss in weight, continuing up to 300 hours, in each case, but the loss with the fine wool was much less than with the others.

	Mean diameter.	Loss in weight as per cent. of initial weight after 300 hours.
	μ	
Merino, fine	20	55
Syrian, coarse	30	77
Persian, coarse	30	82

R. F. I.

Isolation of Carotene from the Suprarenal Glands. O. Bailly and R. Netter. (*Compt. rend.*, 1931, **193**, 961–963.)—Healthy ox-glands were minced and extracted twice with 75 per cent. alcohol containing 2 per cent. of acetic acid in quantities such as to yield an extract of 45 per cent. alcoholic strength, which was then filtered. The sweetbreads were minced, extracted with acetone, the solvent evaporated in a vacuum, and an extract of the dry residue in a 1 : 4 mixture of 33 per cent. potassium hydroxide solution and 95 per cent. alcohol was shaken with petroleum spirit. The bulk of the carotene separated from the alcoholic phase after 48 hours in a vacuum, the yield being 0·1 grm. per 10 kilos. The carotene, which comes *mainly from the cortical and medullary zones of the gland*, appears to be identical with that from vegetable sources; it has m.pt. indefinite at 168 to 169° C. (uncorrected), and the absorption spectrum of a 0·0005 per cent. solution showed the two characteristic bands (*b* between 510 and 525$\mu\mu$, and *F* between 480 and 490$\mu\mu$). There is evidence that the alcoholic extract contains carotene (the crystallisation of which is retarded by impurities), isomerides more soluble than carotene, or a pigment which is gradually converted into it. A connection between the resistance to infection imparted by these glands and by vitamin *A* is indicated. J. G.

Carotenase. Transformation of Carotene into Vitamin *A in Vitro*. H. S. Olcott and D. C. McCann. (*J. Biol. Chem.*, 1931, 94, 185–193.)—Recent work by various investigators has definitely established the rôle of carotene as a precursor of vitamin *A*, and it has been concluded that the conversion takes place in the liver. If an enzyme, carotenase, is responsible for this transformation, it should be possible to prepare vitamin *A* from carotene *in vitro* by incubation with whole liver or liver extracts. The authors describe a series of experiments carried out by them, with this aim in view. The presence of vitamin *A* was detected by ultra-violet absorption spectra methods, since vitamin *A* is characterised by a broad absorption band with a maximum near 328$m\mu$. The liver used was taken from vitamin *A*-free rats. The results show that carotene can be changed into vitamin *A* by incubation with fresh-liver tissue or with an aqueous extract of liver. The agent responsible for the transformation appears to be an enzyme, provisionally called carotenase, since it is destroyed by heat. The conversion of carotene into vitamin *A*, *in vivo*, and the usefulness of ultra-violet absorption spectrum methods for the detection of vitamin *A* are confirmed. It is possible that vitamin *A* is a reduced fragment of the carotene molecule, and that reduction of carotene itself creates that part of the molecule responsible for the absorption at 328$m\mu$. P. H. P.

Growth-Promoting Properties (Vitamin *B* Complex) of the Concentrated Water-Soluble Portion of Milk. G. C. Supplee, O. J. Kahlenberg and G. E. Flanigan. (*J. Biol. Chem.*, 1931, 93, 705–725.)—Data are presented which confirm the investigations of other workers to the effect that acidified water treatment cannot always be relied upon completely to free all commercial caseins from the water-soluble growth-promoting factors. The results also indicate the possibility of a selective adsorption and retention of the different factors of the vitamin *B* complex by caseins prepared by different methods. The meagre evidence shows that further studies are needed on the biological character of caseins used in the determination of certain vitamins. Limited amounts of rice polishings, supplementing a suitable basal ration, supplied white rats with sufficient amounts of the water-soluble maintenance factors to permit of comparable assays of the growth-promoting vitamins. Assurance of the purity and suitability of particular lots of casein is pre-requisite for such determinations. The concentrated water-soluble fraction obtained from milk after the removal of the fat, casein, albumin, and a substantial proportion of the lactose, contains a high concentration of the growth-promoting and antipellagric factors; it contains less of the antineuritic principle (vitamin *B*) than of the other growth-promoting water-soluble factors. The growth response resulting from limited amounts of this milk derivative is increased when extra vitamin *B* (as found in rice polishings) is supplied. Growths induced by the milk vitamin concentrate, either unsuppressed or resumed after suppression, concurrently prevented or alleviated the pellagric symptoms noted. Growth may take place, even though there are wide variations in the proportions of the accessory factors supplied by the water-soluble milk vitamin concentrate and rice polishings. Predictions as to the amount of any one factor required for normal development, without knowledge of the relative amount of the other factors present, are unreliable; all of the known factors must be present to some degree. The autoclaving of a water-soluble milk vitamin concentrate at 120° C. for 5 hours adversely affects its growth-promoting properties. Intensive irradiation with ultra-violet rays for a period of 10 hours has a similar effect; such treatment, however, cannot always be depended upon completely to destroy the growth-promoting factors; this irregularity is probably due primarily to the inefficiency of the irradiation technique. It is shown that accessory water-soluble factors, other than vitamins *B* and *G*, as now defined, may be required during different periods of the life cycle, particularly at, and following, the period of adolescence. Final conclusions as to the existence of such additional factors must await further knowledge of the specificity of the water-soluble factors, and of the ability of the animal to utilise such factors during the different periods of development. According to the work described, irrespective of their final identity and classification, such factors as may be concerned in the maintenance of normal development, through the periods of structural growth and adolescence and beyond, are present in the water-soluble fraction of milk; such factors are thermo-labile at the high temperatures used in the experiments. P. H. P.

Crystalline Vitamin *D*. F. A. Askew, H. M. Bruce, R. K. Callow, J. St. L. Philpot and T. A. Webster. (*Nature*, 1931, **128**, 758.)—Of the four crystalline preparations of vitamin *D* recently described, the one prepared by the authors under the name "calciferol" has been further investigated by the new method involving the preparation of crystalline esters. The product obtained by the action of 3:5-dinitrobenzoyl chloride on the crystalline material in pyridine has been separated into two esters, each of which has been repeatedly recrystallised:—*Calciferyl 3:5-dinitrobenzoate* forms lemon-yellow plates, melting at 145°–147° C., and having $[\alpha]^{20}_{5461}$ + 104° in acetone, $[\alpha]^{20}_{5461}$ + 68° in benzene. On hydrolysis it yields *calciferol*, with m.pt. 114·5°–117° C., $[\alpha]^{20}_{5461}$ + 119·5, $[\alpha]^{20}_{D}$ + 105° in alcohol, $[\alpha]^{20}_{5461}$ + 99°, $[\alpha]^{20}_{D}$ + 81° in acetone, antirachitic activity 40,000 International Units per mgrm.; the solution in alcohol has an intense absorption band with a maximum of $\epsilon = 46{\cdot}0$ at 265*mμ*. *Pyrocalciferyl 3:5-dinitrobenzoate* forms orange prisms with m.pt. 167·5°–169·5° C., $[\alpha]^{20}_{5461}$ + 250° in benzene, yields *pyrocalciferol*, which has m.pt. 92°–94° C., $[\alpha]^{20}_{5461}$ + 608°, $[\alpha]^{20}_{D}$ + 494° in alcohol, has no antirachitic activity, but shows an absorption band with maxima of $\epsilon = 15{\cdot}7$ at 296*mμ*, 27·1 at 284*mμ*, and 26·1 at 274*mμ*.

Both calciferol and pyrocalciferol have the same empirical formula as ergosterol, and the supposition that calciferol is a direct product of the irradiation of ergosterol has been confirmed by the preparation of the dinitrobenzoate directly from the undistilled crude irradiation product. D. G. H.

Dermatitis from Oranges and Lemons. S. G. Horner. (*Lancet*, 1931, **221**, 961–962.)—A dermatitis, often of a disabling degree, was found to affect a number of workers preparing oranges and lemons in the marmalade season, and the "peelers" were more affected than the workers dealing with the fruit juices, notwithstanding the fact that in the case of the former there was practically no contact with the juice. Although among "peelers" there is predisposition to injury through accidents with knives and other implements, and friction of the wrists and forearms, it seemed probable that there is a more aggressive irritant in the peel of the fruit than the citric acid of the fruit hearts, and it is suggested that the limonene present in lemon and orange oils is the irritant. If the exposed skin was oiled before beginning work, injury was very rarely sustained, owing to prevention of damage to the horn cells from immersion in water, so that these remained healthy and resisted the action of limonene and citric acid. D. G. H.

Bacteriological

Pathogenic Fungus on Wool Cloth. A. G. Gould and E. K. Carter. (*Amer. J. Hyg.*, 1931, **14**, 694.)—An old woollen jersey, saturated with stale human perspiration, was cut into a number of one-inch squares, and upon each was placed a particle of a fresh culture of *Tricophyton interdigitale*, care being taken that none of the medium itself was transferred. A particle was also placed in a sterile Petri dish. The squares of cloth and the Petri dishes were incubated, sterile water being added daily to all. At intervals over two months, inoculations were made on nutrient media from the growth itself, and also from the piece of cloth from which the growth had been removed, so far as was possible. From the growth, positive results for *T. interdigitale* only were obtained, and from the cloth almost invariably a non-pathogenic fungus developed without *T. interdigitale.*

The authors conclude that, although the pathogenic organism was alive at the end of the period, there was no evidence of development. R. F. I.

Agricultural

Determination of Plant Ash Constituents in the Presence of Silica. J. Davidson. (*J. Assoc. Off. Agric. Chem.*, 1931, **14**, 551–558.)—Wheat and rice straws, grown with and without fertilisers, have been analysed for total and acid-soluble ash, silica, phosphorus, potassium, calcium, magnesium, iron and aluminium, and manganese. When the ash of the straw was dissolved in dilute hydrochloric acid, without previous volatilisation of silica, the results of analysis were too low in every case. Digestion of the acid-insoluble residue with hydrofluoric and sulphuric acids to expel the silica, with subsequent re-solution in dilute hydrochloric acid, yielded additional quantities of the ash constituents. When the ash was digested directly with hydrofluoric and sulphuric acids, and then dissolved in dilute hydrochloric acid, the results agreed with the sum of the respective results obtained from the solutions of the ash and the insoluble residue after digestion with hydrofluoric and sulphuric acids, except for the acid-soluble ash and silica. The exception in these cases is due to the conversion of the bases into sulphates, rendering the results for acid-soluble ash too high and those for silica too low.

Volatilisation of silica, or possibly some other procedure to prevent retention of bases by the acid-insoluble residue, is essential for the proper analysis of ash constituents of plant substances rich in silica. It is recommended that the acid-soluble ash in plant substances rich in silica be determined, as well as the total ash, when analyses of the ash constituents are omitted.

The mechanism by which a soluble portion of ash constituents is held in the acid-insoluble residue cannot be determined from the data at hand. The fact that the variations in silica content have no effect on the magnitude of the retention does not point to adsorption. On the other hand, the fact that retention tends to increase with the concentration of the acid-soluble ash constituents, is in agreement with adsorption phenomena. T. H. P.

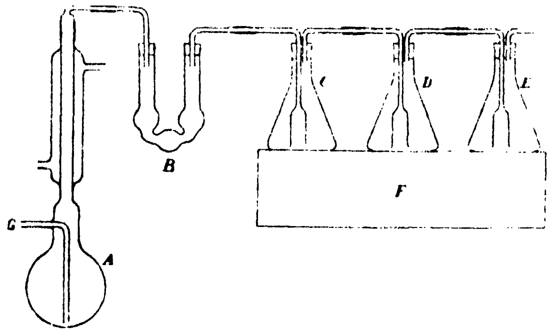
Colorimetric Methods for the Determination of Manganese in Plant Materials. J. Davidson and R. G. Capen. (*J. Assoc. Off. Agric. Chem.*, **1931, 14,** 547–551.)—Determinations of manganese in plant materials and inorganic manganese compounds have been made by the potassium periodate (*cf.* Davidson and Capen, *J. Assoc. Off. Agric. Chem.*, 1929, **12**, 310), ammonium persulphate (*cf.* Newcomb and Sankaran, ANALYST, 1929, **54**, 348), and sodium bismuthate (*cf.* Gortner and Rost, *J. Ind. Eng. Chem.*, 1912, **6**, 522) colorimetric methods, and by the gravimetric method. The first two of these methods are equally suitable for plant materials, but the sodium bismuthate method gives appreciably lower results. Ammonium persulphate is much cheaper than potassium periodate, but, when the plant materials contain an appreciable quantity of chlorides, the ash must be ignited with sulphuric acid to expel the chlorine if the persulphate method is to be used, whereas chlorides (as distinguished from hydrochloric acid) do not interfere with the periodate method. The gravimetric method is found to be inaccurate for determining manganese in plant materials. T. H. P.

Water Analysis

Determination of Organic Carbon in Sewage. E. V. Mills. (*J. Soc. Chem. Ind.*, **1931, 50, 375–377**T.)—The usual methods for the determination of organic carbon in sewage are subject to two defects: loss of organic matter in the preliminary treatment and serious lack of sensitivity. The following procedure eliminates the first source of error and results in greatly improved accuracy:

The reaction flask A is of 250 c.c. capacity and the reaction products pass through the fused-on condenser to B, which contains saturated aqueous chromium trioxide to remove oxides of sulphur, and then through C, D and E, each containing 100 c.c. of carbonate-free baryta solution (10 grms. per litre); a soda-lime tube on the gas-exit tube prevents diffusion of carbon dioxide from the atmosphere into E. The baryta flasks stand on a water-bath F.

Into A, immersed in cold water, are placed 50 c.c. of the sewage and, cautiously, 150 c.c. of concentrated sulphuric acid. Air free from carbon dioxide is passed through this mixture for 15 minutes, dissolved and inorganic carbon dioxide being thus expelled; 0·5 c.c. of saturated silver nitrate solution and 10 c.c. of saturated chromium trioxide solution are next added to the flask, which is then connected with B. The air stream is shut off by a clip at G and the contents of the reaction flask are heated by a naked Bunsen flame until a brisk evolution of gas occurs; the reaction mixture should not boil. With the proportions of water, acid and chromium trioxide given, a homogeneous mixture is formed, and excess of the trioxide remains after the oxidation; moreover, the evolution of oxides of sulphur is minimised and such oxides should not reach the absorption flasks. The end of the absorption of carbon dioxide is shown by the settling of the precipitate and the clearing of the baryta solution in all three absorption flasks; the last of these should show little or no precipitate. The flasks are removed and allowed to cool with a soda-lime tube at each end, the contents being then filtered through a weighed Gooch crucible, on which the whole of the precipitate is thoroughly washed with boiling water; six fillings of the crucible, with slow filtration, usually suffice to remove all but traces of the baryta. The crucible is then dried and weighed, the weight being corrected in accordance with the result of a similar determination on the reagents alone. In order to correct for any small amount of oxides of sulphur which may have been absorbed, the weighed precipitate is washed with bromine water, first neutral and then acidified with hydrochloric acid. The combined washings are boiled, left for a time, and filtered, the barium sulphate formed being washed and weighed as usual. With careful working, this sulphate does not weigh more than 1 mgrm. and may, indeed, be disregarded.



The 3 : 1 acid to water ratio may be diminished somewhat if phosphorus pentoxide is mixed with the acid. By the above method, malonic acid gave 100·95 per cent. of its organic carbon as the mean of four determinations, with a maximum deviation of 0·3 from the mean, and sucrose 99·98 per cent. with maximum deviation 0·2 from the mean of three determinations. T. H. P.

Organic Analysis

Quantitative Determination of Acetic Acid in Cellulose Acetates. E. Berl, G. Rueff, W. Wahlig. (*Chem. Ztg.*, 1931, 55, 861–862.)—The available processes are reviewed, and it is concluded that they are neither as rapid nor as accurate as desired. In the new process proposed, which occupies an hour and a half, the cellulose acetate is hydrolysed in phosphoric acid; the acetic acid liberated is distilled in steam, and the distillate is titrated with baryta. *Apparatus.*—This consists of (*a*) a steam generator—a 1-litre flask, containing dilute baryta solution, fitted with a safety tube and a leading tube, (*b*) a distilling flask (250 c.c. capacity) fitted with a ground-glass stopper, carrying a leading tube passing nearly to the bottom of the flask, and an exit tube provided with a splash-bulb, (*c*) a long Liebig condenser, with which the exit from the splash-bulb is connected by a ground-glass joint, (*d*) a receiving flask for the distillate. *Method.*—The carefully dried sample (0·5 grm.) is introduced into the distilling flask, and 20 c.c. of phosphoric acid (89 per cent.) are added; the stopper of the flask is placed in position, and the flask is placed in boiling water and gently shaken for 15 minutes, *i.e.* until the sample has completely dissolved. Five c.c. of water are then added to the contents of the flask, from a pipette, by way of the leading tube. The flask is connected with the other parts of the apparatus, and the steam-distillation is carried out until about 450 c.c. of distillate have been collected, when the volume of liquid in the distilling flask should be from 75 to 100 c.c.; about one hour is required for the steam-distillation. The distillate is titrated with $N/5$ baryta solution, phenolphthalein being used as indicator. S. G. C.

Esters as Adulterants of Cassia Oil and their Detection. J. Callaway and T. N. Bennett. (*J. Assoc. Off. Agric. Chem.*, 1931, 14, 571–573.)—In the U.S.P., *X*. it is specified that cinnamon or cassia oil shall contain at least 80 per cent. by volume of cinnamaldehyde, as determined by the neutral sodium sulphite method. Tests are outlined for such common adulterants as heavy metals, rosin or rosin oil, and chlorinated products, the last indicating the addition of synthetic cinnamaldehyde. In carrying out the U.S.P., *X*. assay method for cinnamaldehyde, so much 5 per cent. sodium bisulphite solution is necessary to maintain neutrality that the total volume exceeds 100 c.c.; replacement of the 5 per cent. by a saturated solution is recommended. The tests for rosin (oil) and heavy metals are fairly satisfactory with crude oils from China, but, since synthetic cinnamaldehyde free from chlorine is now available in European markets at a lower price than the oil, a more reliable test for this product is needed.

Adulteration of the oil with synthetic cinnamaldehyde would necessitate addition of non-aldehydes to render the proportion of cinnamaldehyde normal. The non-aldehyde residue (about 1·5 c.c.) remaining, after determining the cinnamaldehyde by the U.S.P. assay method, was, therefore, examined. The clear residue was heated on a boiling water-bath in a test-tube with about 3 c.c. of a 10 per cent. solution of potassium hydroxide in absolute alcohol for 2 or 3 minutes. The presence of foreign esters (other than cinnamyl acetate) was revealed by the formation of a precipitate which was usually sufficient to cause complete solidification. This test gave negative results with every one of a large number of crude oils, whereas various commercial redistilled oils yielded positive results, and the precipitates were found to contain esters of benzoic and phthalic acids. Although these acids have been reported as constituents of cassia oil, they should be dissolved in the aqueous solution, probably as sodium salts, during the treatment with the neutral sulphite, and hence should not interfere with this test. T. H. P.

Preparation and Determination of Acrolein. E. V. Zappi and R. A. Labriola. (*Anal. Asoc. Quim. Argentina*, **1930**, **18**, 243–246.)—Various modifications are suggested for improving the method of preparing acrolein given by Gilman (*Organic Syntheses*, Vol. VI, 1926, 1). Acrolein exhibits great tardiness in reacting with hydroxylamine, and the method described by Sudborough and James (*Practical Organic Chemistry*, 1920, 225) for the determination of aldehydes is quite inapplicable in this case.

The method recommended is based on that of Ivanov (*Arch. Hyg.*, **73**, 307), and depends on the fixation of sodium bisulphite by the aldehyde. The solutions used are prepared by (1) dissolving 5 grms. of potassium iodide in the minimum quantity of water, adding 4·8 grms. of resublimed iodine, making up to 1000 c.c., and, after titrating with 0·1 *N* sodium thiosulphate solution, diluting with water, so that 10 c.c. of the final solution correspond with 3·49 c.c. of 0·1 *N* thiosulphate; (2) diluting 6 c.c. of commercial 30 per cent. sodium bisulphite solution to 1000 c.c. and adjusting the volume so that it corresponds with solution (1). The acrolein to be determined should be dissolved in 96 per cent. alcohol, and the solution should contain not more than 1 mgrm. per c.c. Ten c.c. of the acrolein solution, prepared by weighing, are treated with 15 c.c. of solution (2), and the whole is left in a cool dark place for 6 hours, after which the excess of bisulphite is determined by titration with the iodine solution [1 c.c. of solution (2) is equivalent to 0·001 grm. of acrolein]. Treatment of the acrolein, in chloroform or carbon tetrachloride solution, with bromine and subsequent determination of the excess of bromine, gives less accurate results than the above procedure. T. H. P.

Reduction of the Bromine Derivatives of Fatty Acids. W. Kimura. (*J. Soc. Chem. Ind., Japan*, 1931, **34**, 355B.)—The method recommended is a modification of that of Rollet. The bromide is boiled with zinc and methyl alcohol, during which 5 *N* sulphuric acid is added, drop by drop. After cooling, the methyl ester of the unsaturated fatty acids is extracted with petroleum spirit. The reduction of tetra- and hexabromides is simple, but that of the decabromide is difficult, and a low yield is obtained. R. F. I.

Inorganic Analysis

Iodimetric Determination of Ferric Iron. E. Rupp. (*Z. anal. Chem.*, 1931, **86**, 217–219.)—The method is based upon conversion of the iron into ferricyanide, and its reaction with iodide: $K_3Fe(CN)_6+KI=K_4Fe(CN)_6+I$. The solution, containing not more than 0·1 grm. of iron as ferrous or ferric iron, or both, is treated with 10 c.c. of 25 per cent. phosphoric acid, 10 per cent. ammonia, (until the reaction is distinctly alkaline), water to bring the volume to 100 c.c., and 1·5 to 2 grms. of pure potassium cyanide. The liquid is heated until the colour of the solution has just changed from brown to a clear greenish-yellow, the heating being interrupted as soon as the colour change is complete. When cold, the solution is acidified with 30 c.c. of dilute sulphuric acid and titrated with 1 per cent. permanganate solution, the resulting slight pink colour being discharged with a tiny crystal of oxalic or tartaric acid. The solution is next treated with a minimum of 0·3 grm. of potassium iodide and with zinc sulphate (2 grms.); after

3 minutes' standing, the iodine is titrated with 0·1 N thiosulphate solution, with starch as indicator. Three minutes after the conclusion of the titration, any after-blueing is removed by continued titration. The operation requires about 30 minutes. The method is applicable in presence of manganese, chromium, aluminium, magnesium, tin, and lead, whilst copper, cadmium, nickel, and zinc interfere. W. R. S.

Determination of Oxygen and Nitrogen in Iron and Steel by the Vacuum Fusion Method. H. C. Vacher and L. Jordan. (*Bureau of Stds. J. Research,* **1931, 7, 375–401.**)—This paper contains the results of an extended study of the vacuum-fusion method for the determination of gases in steel, and a full description of the apparatus and method now adopted at the Bureau of Standards is given. On account of the highly-specialised nature of these determinations reference to the paper for working details is essential. S. G. C.

Antipyrine as a Reagent for Cobalt. K. Woynoff. (*Chem.-Ztg.,* 1931, **55**, 914.)—Whereas the addition of antipyrine to a solution of a cobalt salt gives rise to no distinctive colour-change, it is claimed that a characteristic blue colour is produced when the mixed solution is made to dry on filter paper, and this has been made the basis of the following spot test.—A strip of filter paper is saturated with the solution to be tested, and dried (the author recommends employing an electrically-heated plate). One drop of antipyrine solution (20 per cent.) is placed on the strip, which is then dried again. The formation of a blue ring on the paper denotes the presence of cobalt. The blue ring remains stable when the strip is subsequently cooled only when there is more than 0·6 mgrm. of cobalt chloride in 1 c.c. of the test solution; with a lower concentration of cobalt, the blue ring is only visible when the strip is warm; the test fails altogether when less than 0·3 mgrm. per c.c. of cobalt chloride is present. Nickel, mercury, magnesium and the alkaline earth metals do not interfere, but iron and copper mask the test by giving a brown and a yellow colour, respectively.

S. G. C.

New Colorimetric Method for the Determination of Potassium. H. R. D. Jacobs and W. S. Hoffman. (*J. Biol. Chem.,* 1931, **93**, 685–691.)—The formation of a hitherto unmentioned, stable, coloured compound of cobalt (prepared from cobalt, choline and ferrocyanide) and its application to the micro-determination of potassium in biological fluids is described. A solution of sodium ferrocyanide added to a mixture of a cobaltous salt and choline hydrochloride in aqueous solution gives an emerald-green colour immediately. Preliminary experiments showed that the colour is sensitive to minute amounts of cobalt, choline and ferrocyanide, and that, in the presence of a given excess of choline and ferrocyanide (*vide infra*), it can be used to determine colorimetrically small variations in the concentration of cobalt. The coloured solution can be diluted with water without affecting its quality; the colour develops to maximum intensity in a few minutes and maintains this intensity for hours. The usual method for the determination of potassium in the blood and the urine depends upon the precipitation of the element as the cobaltinitrite, and the subsequent determination of one of the constituents of the precipitate. The procedure outlined for the determination of potassium in blood, urine and ash solutions, by means of the new colour, is as follows: —The potassium is precipitated from blood serum by the method of Kramer and Tisdall (*J. Biol. Chem.*, 1921, **46**, 339). Into a 15 c.c. conical centrifuge tube, marked at 6 c.c., is pipetted 1 c.c. of serum, and 2 c.c. of Kramer and Tisdall's sodium cobaltinitrite reagent are added, slowly, with constant shaking. After 45 minutes, 2 c.c. of water are added, and the tube is centrifuged at moderate speed for 15 minutes. The tube is inverted and drained briefly, 1 c.c. of water is run down its side, it is centrifuged for 5 minutes, and again inverted, and drained. The precipitate is suspended in 2 c.c. of 70 per cent. alcohol with the aid of a stirring rod, the tube centrifuged for 5 minutes, inverted, and drained. The alcohol washing is repeated once. After it has drained, the precipitate is suspended in 1 c.c. of water. Another c.c. of water is added, and the tube is immersed, with occasional shaking, in a boiling water-bath, for 10 minutes. The precipitate dissolves to form a clear, colourless solution. A small amount of insoluble material, probably protein, does not interfere. When the tube has cooled, 1 c.c. of 1 per cent. choline hydrochloride and 1 c.c. of 2 per cent. sodium ferrocyanide are added to the solution, which is then made up to the 6 c.c. mark. The precipitation of potassium from inorganic solutions or solutions of ash is made from 2 c.c. of unknown solution with 1 c.c. of reagent. The first washing with water is omitted, and the precipitate is washed twice with 70 per cent. alcohol, as outlined for serum, and the remainder of the procedure is the same. The coloured solution formed is compared with a standard coloured solution made from 1 c.c. of standard cobalt nitrate (or sulphate), 1 c.c. of 1 per cent. choline hydrochloride, and 1 c.c. of 2 per cent. sodium ferrocyanide made up to 6 c.c. with water. The standard cobalt solution is either 0·6701 grm. of $Co(NO_3)_2.6H_2O$ or 0·6469 grm. of $CoSO_4.7H_2O$, made up to 1 litre with water. These solutions are standardised against standard potassium sulphate solution containing 0·4011 grm. of potassium sulphate per litre (equivalent to 18 mgrms. of potassium per 100 c.c.), which is treated in the manner described above. The colours are easily matched in any good colorimeter. The results of determinations of potassium in blood sera, in urine, and in inorganic solutions are given. Ammonium salts interfere with the determination, and hence fluids such as urine should first be evaporated and the residue ashed. P. H. P.

Volumetric Determination of Sulphates by the Use of Benzidine Solution. S. Snyder. (*Chemist Analyst*, 1931, **20**, VI, 8–9.)—Phosphates should first be removed by dilution of a volume of sample containing about 10 mgrms. of sulphur (as sulphate) to 50 c.c., and addition of concentrated ammonia until the liquid turns faintly pink with phenolphthalein. Ten c.c. of 5 per cent. ammonium chloride solution and 1·5 grms. of magnesium carbonate are then added, and the mixture is diluted to 100 c.c., shaken, and filtered, after 30 minutes, through a dry paper. *Inorganic sulphate.*—*N*-Hydrochloric acid is added to 5 c.c. of the filtrate containing 2 drops of a 0·04 per cent. solution of bromphenol blue in alcohol, until a yellow colour is obtained (*p*H 4); 2 c.c. of a filtered solution of 4 grms. of benzidine in 250 c.c. of water containing the equivalent of 50 c.c. of *N* hydrochloric acid are then added, and followed, after a few minutes, by 4 c.c. of 95 per cent.

acetone. After 10 minutes the benzidine sulphate is filtered off in a glass tube. which is 7 cm. long, and 15 mm. in diameter at the top end, and has a hole (3 mm. in diameter at the bottom), which is plugged with a filter mat. The precipitate is washed with 3 1-c.c. portions of the acetone, and the filter tube and contents are then placed in boiling water. A few drops of phenol red are added, and the solution is titrated, while hot, to a definite pink colour with 0·02 *N* sodium hydroxide solution (1 c.c.$\equiv$0·32 mgrm. S.). *Total Sulphate.*—The filtrate (5 c.c.) from the phosphate precipitate is evaporated with 1 c.c. of 3 *N* hydrochloric acid, the residue is heated on the bath for 10 minutes, and the above procedure is followed. *Ethereal Sulphate* is obtained by difference. *Total Sulphur.*—Five c.c. of the original filtrate are evaporated with 0·5 c.c. of a solution containing 20 grms. of copper nitrate and 5 grms. of potassium chlorate per 100 c.c. (Benedict), and the residue is gently ignited and then evaporated with 3 c.c. of 2 *N* hydrochloric acid. The above procedure is then followed, except that the strength of the acetone should be 50 per cent. The method is specially recommended for urine and water analyses (*cf.* Rosenheim and Drummond, ANALYST, 1914, 39, 319). J. G.

Microchemical

Detection of Glucosides in Plant Tissues. A. Niehhammer. (*Mikrochem.*, 1931, 9, 136–142.)—Several glucosides were identified by sublimation under reduced pressure, by observing the temperature of sublimation and the appearance, crystalline form and chemical reactions of the sublimate. There is sometimes slight decomposition on subliming, but this does not interfere with most of the tests. Sections of biological tissue, as well as the substance itself, may be used for the sublimation, which is carried out in a Klein-Werner apparatus (G. Klein, *Praktikum der Histochemie, Vienna,* 1929), heating on an oil-bath for low temperatures, and a sand-bath for high temperatures. The sublimate is collected on a small cover glass attached to the cooler with anhydrous glycerin. *Aesculin,* or a slice of the bark of horse chestnut trees containing the glucoside, or the concentrated alcoholic extract, gives a sublimate under reduced pressure at 260° C. When sublimed at 330° C. for one or two hours fine crystals are formed, which, with Reinecki's salt ($NH_4[Cr(NH_3)]_2(SCN)_4$), give typical branch-like crystals. With bromine in potassium bromide solution, aesculin gives typical black, star-like crystals; the sublimate darkens without crystal formation, probably owing to slight decomposition on sublimation. The reaction with bromine may also be used on sections of the tissue. *Rhinanthin* is present in the seeds of some grasses and cereals. When a section of tissue coating the glucoside is heated for $\frac{1}{2}$ to 1 hour to 320° C., it gives a crystalline sublimate; when heated to 400° C., or higher, the sublimate consists of small drops of oil, containing some crystals and powder. The sublimate obtained at 320° C. does not saponify with saturated alcoholic potassium hydroxide solution, but that obtained at 400° C. is easily saponified, and then gives typical rosettes of crystals. The sublimate obtained at 320° C. gives characteristic crystals with bromine in potassium bromide solution; the same crystals are not easily distinguished when the test is carried out in the tissue, but are obtained from the alcoholic extract of the seeds or from the expressed sap.

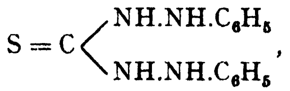
The sublimate obtained at 420° C. gives characteristic crystals with bromine which may be distinguished among the distributed particles of the oil, or, if the saponified sublimate is used, among the products of saponification. *Syringin* is found in the bark and leaves of the lilac. When a section of the bark, or its concentrated alcoholic extract, is heated to about 360° C., the sublimate consists of needle-shaped crystals. When the aqueous extract, after removal of proteins with lead acetate, is treated with bromine in potassium bromide solution, the formation of crystals and of a dark precipitate is observed. Sections of bark tissue give the same crystals when treated with bromine in potassium bromide solution. *Saponarin* is found in the leaves of the common elder. The pure substance or leaves, or their pyridine extract, when sublimed in the usual way at reduced pressure at 360° C., give fine needles, similar to those from aesculin. The glucoside gives a yellow solution with alkalis and a blue colour with iodine in potassium iodide solution. *Digitonin*, from digitalis, can be sublimed at 360° C., giving fine needles. With bromine, crystals similar to those obtained with rhinanthin are formed. *Salicin*, from the bark of willow trees, sublimes at 360° C., giving fine needle-shaped crystals.

J. W. B.

Micro-chemical Examination of Glucosides. L. Rosenthaler. (*Mikrochem., Pregl-Festschrift.*, 1929, 302–307.)—Tests on the glucosides are carried out, using a combination of physical (melting-point determination, refractive index) and chemical methods. When the test is applied to tissue or biological material it is always necessary to make a control test for comparison on a similar sample, but with the glucoside removed by a suitable solvent. The various methods are:—(1) *Hydrolysis*, followed by the identification of the aglucone by hydrolysis with enzymes, is the most generally suitable for biological material. Hydrolysis with acid is used when the aglucone is insoluble in water, that is, for salicin and saponin, digitalis and strophanthus glucosides. Micro-sublimation is used for arbutin, which decomposes, giving its aglucone, which can be identified in the sublimate. (2) *Colour Reactions* generally apply also to carbohydrates, which should not be present. Concentrated sulphuric acid tends to destroy tissue, and is better used diluted with water or alcohol. For colour reactions with alkalis, concentrated aqueous or alcoholic potassium or sodium hydroxide is used. For distribution tests on tissues gaseous ammonia may be used. Reactions with ferric chloride are not usually sufficiently sensitive, and the reagent is unsuitable for tests on the distribution of glucosides in tissues. Nitric acid should be diluted for use with tissues. (3) *Precipitation Reactions.*—The precipitation reagents for the glucosides of high molecular weight are: tannin, hydrobromic acid, silico-molybdic acid, and similar substances; these also precipitate proteins and alkaloids, which should not be present. Ammonium sulphate also precipitates glucosides from their aqueous solutions. Special precipitation reagents include metal salts and salts of alkaline earth metals for glucosides of acid properties, such as saponin, which is precipitated by lead acetate or baryta water; these reagents also precipitate salts of organic acids. In tissues which adsorb the heavy metals it is not always possible to confirm the formation of the salt of the glucoside, after washing out the reagent, by precipitating the heavy metal with hydrogen sulphide. Stearin is a precipitant for digitonin and other glucosides similar to saponin. In tissues, the precipitation does not always occur in the original position of the glucoside, but usually at the border of the section. Nitroso-dimethylaniline is sometimes used for the phenyl-glucosides, such as arbutin, which gives a characteristic addition product. Chlorine or bromine derivatives which are slightly soluble, may be used to identify the glucoside or aglucone. For distribution tests in tissues the halogen should be used in gaseous form. (4) *Biological Reactions.*—An example is the solution of red blood corpuscles by haemolysing glucosides. No other haemolysing substance should be present. J. W. B.

Specific "Spot" Test for Mercurous Ion. N. A. Tananajin. (*Ukrainski chemitschni Shurnal,* 1930, 5, 63–4; *Mikrochem.,* 1931, 9, 95.)—A drop of saturated sodium nitrite solution is placed on a filter paper, and a small drop of the test solution is put in the middle, while the paper is still moist. A brown fleck indicates the presence of mercury. The test is specific for mercurous ions, the smallest amount recognisable being 0·2γ of mercury in a dilution of 1 : 10,000. The presence of coloured cations, such as chromium, iron and cobalt, reduces the sensitiveness. J. W. B.

Use of Diphenylthiocarbazide for the Detection of Magnesium. P. Agostini. (*Annali Chim. appl.,* 1930, 20, 235–238; *Mikrochem.,* 1931, 9, 96.)—This "spot" test may be carried out on a "spot" plate, or on a filter paper impregnated with the reagent. When two drops of a cold, saturated alcoholic solution of diphenylthiocarbazide are added to a drop of the test solution, and then excess of ammonia is added, a red gelatinous precipitate, or a red coloration, is formed in the presence of magnesium. The reaction is specific for magnesium, which may be detected in a dilution of 1:300,000. The reagent,



$$S = C\begin{cases} NH.NH.C_6H_5 \\ NH.NH.C_6H_5 \end{cases},$$

is formed by the action of carbon disulphide on phenylhydrazine. J. W. B.

Micro-Determination and Separation of Calcium and Magnesium. K. L. Maljaroff. (*Mikrochem.,* 1931, 9, 132–135.)—The method is applicable to the determination of about 10 mgrms. of calcium and magnesium, when present as carbonate, oxide or hydroxide. The mixture must contain none, or not more than a trace, of the alkali carbonates. The method is designed for the analysis of natural and artificial carbonates and oxides, such as magnesite, dolomites and technical calcium and magnesium carbonates. The separation utilises the different solubilities of the oxides in water. *Method.*—The powdered sample is ignited in a platinum crucible for about 20 to 30 minutes, to drive off organic matter, to render the iron and aluminium insoluble, and to convert the calcium and magnesium into oxides. The crucible is cooled in a desiccator over soda-lime, and the contents are then transferred to a conical flask, about 60 to 80 c.c. of water (free from carbon dioxide) being used to dissolve all the calcium oxide. The mixture is rapidly heated to boiling, and filtered rapidly through a small, quick-filtering filter paper. The precipitate is washed by decantation with small amounts of water. The filtrate is titrated with 0·05 to 0·2 *N* acid, methyl orange being used as indicator. The acid used is equivalent to the calcium oxide. The filter is added to the precipitate, and the magnesium oxide is dissolved in a small excess of 0·05 to 0·2 *N* acid, with slight heating, and the excess acid is titrated against sodium hydroxide solution, methyl orange being used as indicator. The acid used is equivalent to the magnesium oxide. When sulphuric acid is used for the titration the iron and aluminium oxides do not dissolve. Comparative analyses of dolomite and magnesite on the micro scale, and on the macro scale (calcium being weighed as oxalate and magnesium as phosphate), gave excellent agreement. Artificial mixtures of calcium and magnesium carbonate analysed gave differences between calculated and found percentages of less than ±0·3 per cent. J. W. B.

"Spot" Test for Nitrites. F. L. Hahn. (*Mikrochem.*, 1931, 9, 31–33.)—The diazo reaction is used as a "spot" test for identifying nitrites. The sensitiveness of the test has been increased by improving the preparation of the impregnated filter papers, so that the smallest amount recognisable is $2{\cdot}5-5{\cdot}0\times10^{-5}\gamma$ and the limit of dilution is 10^{-7}. The naphthylamine oxalate reagent is prepared by dissolving one part of oxalic acid in alcohol on the water-bath, and then adding one part of α-naphthylamine, dissolved in a little alcohol. After cooling, the crystals that separate are filtered off, washed with alcohol and ether, and dried in a vacuum over potassium hydroxide; they are kept protected from laboratory air, which always contains nitrous acid (from Bunsen burners). Before impregnating the filter paper it must be cleaned by steaming as follows:—The filter paper is hung from a platinum hook, inside a large test tube, supported from the stopper, and the tube is heated on a water-bath while a current of steam is passed through it for 5 minutes. A solution of 1 grm. of α-naphthylamine oxalate and 1 grm. of pure sulphanilic acid and 0·2 grm. of potassium oxalate in 100 c.c. of hot distilled water is sucked into the test tube containing the filter paper until the paper is covered, when the impregnating solution is removed by means of a delivery tube which reaches the lowest part of the test tube. The tube is still kept on the water-bath, and the filter paper is dried inside it in a stream of clean air that has been passed through soda-lime and sulphuric acid. The filter papers thus prepared are colourless before the test, and are coloured red by nitrite. J. W. B.

Physical Methods, Apparatus, etc.

Immersion Liquids for Refractive Index Determinations. A. Mayrhofer. (*Mikrochem.*, 1931, 9, 52–71.)—Instead of a large number of immersion liquids of varying refractive powers, it is suggested that a small number of liquids should be used in mixtures of varying proportions. Mixtures of low refractive index, large range, stability on keeping, and comparative chemical inertia are:—Water and glycerin: range, 1·333–1·465; cineole and paraffin oil: range, 1·456–1·482; paraffin oil and α-mono-bromnaphthalene: range, 1·482–1·658. High refracting mixtures include:—Paraffin oil and bromoform: range, 1·482–1·597; bromoform and α-mono-bromnaphthalene: range, 1·597–1·658; and bromoform and iodide: range, 1·658–1·740. These were used chiefly for testing the standard mixtures by dilution. The volumes of the different constituents of the mixtures were measured by means of micro-burettes. There was excellent agreement between the calculated refractive index of the mixtures from the volumes and refractive indices of the two constituents, and that found by measurement. Even after keeping for four years the mixtures remained almost unaltered.

J. W. B.

Quantitative Spectrographic Analysis. A. Schleicher and J. Clermont. (*Z. anal. Chem.*, 1931, **86**, 191–216, 271–288.)—The methods of quantitative spectrographic analysis, as applied to the examination of commercial metals, are discussed; the authors give preference to Gerlach and Schweitzer's "absolute" method over Hartley and de Gramont's, based on observation of the "ultimate" lines. The papers deal with the determination of tin in lead, and of titanium, silicon, and iron in technically pure aluminium. For details reference should be made to the original papers. W. R. S.

Reviews

THE SOIL AND THE MICROBE. By SELMAN A. WAKSMAN and ROBERT L. STARKEY. Pp. 250. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1931. Price 17s. 6d.

The scope of this work is indicated in the sub-title, "An Introduction to the Study of the Microscopic Population of the Soil and its Rôle in Soil Processes and Plant Growth," and, in accordance with this, the authors employ the term "microbe" in its widest sense. The subject matter extends from filterable viruses to earthworms, though the treatment mainly deals with the bacteria, actinomyces and fungi, with some consideration of the protozoa. The general relations between the soil and the plant on the one hand, and the microbial population on the other, are considered in the first three chapters. Chapters IV to VII deal, respectively, with the decomposition of organic matter in the soil, the fixation of nitrogen and ammonification, nitrate formation and reduction, and the transformation of mineral substances. The associations between soil organisms and the higher plants occupy Chapter VIII, and the effects of soil treatment on the micro-population are treated in Chapter IX. The final chapter brings the matter of the earlier chapters into relationship.

Generally, the book is well written and readable. The text is illustrated by 85 figures and diagrams and 56 tables from authoritative sources; the value of the figures, however, would have been greatly increased had the authors indicated the magnifications. Though the sources of the illustrations are acknowledged, the very few names mentioned in the text appear to have been left in by oversight. Loose writing occurs occasionally; as an example, "Each plant seems to be quite capable . . . of transforming sunlight into available food . . ." (p. 181) may be quoted.

The treatment throughout is naturally, from the size and scope of the book, very generalised. It should appeal to the student of agriculture and to the general reader, for whom it appears to be intended. There is no bibliography, but at the end of each chapter there is a short list of text-books dealing with the subject considered.

F. E. DAY.

RECENT ADVANCES IN ORGANIC CHEMISTRY. By ALFRED W. STEWART, D.Sc. Vol. I. Pp. 428. Vol. II. Pp. 432. Sixth Edition, Revised and Enlarged. London: Longmans, Green & Co., Ltd. 1931. Price, 21s. net per vol.

This book, in its main outlines, is now fairly well known, seeing that a sixth edition has been called for. The present volumes follow on the lines of their predecessors, the text having swollen by some ninety pages, owing to the inclusion of some new information on large ring compounds, strainless carbon rings, di- and tri-terpenes and the stereochemistry of diphenyl compounds. Extensive revision has resulted in the chapters on carbohydrate constitutions and anthocyanins, containing an account of much recent work which has been done in these important and interesting branches of organic chemistry. Nevertheless, in spite of much revision and of the volumes bearing the date 1931, it may be questioned whether the work of the last ten years receives adequate attention.

Many readers of the Journal of the Chemical Society will be surprised to read that "Up to the present, the full implications of the Lewis atom have not been whole-heartedly applied in the field of organic chemistry, as the matter is a complex one; but, possibly, before long, something will be done in this line of thought" (Vol. I, p. 17). Their surprise will not be lessened when, on coming to the chapter on "Orienting Influences in the Benzene System," they fail to find the names of Debye and Ingold, or any reference to the work of Robinson later than 1922. In the opinion of the reviewer, the chapter on "Some Applications of Electronics to Organic Chemistry" is hesitant and out of date. The amplification of this section would, to a large extent, render unnecessary the chapter on "Structural Formulae and their Failings."

The concluding sentence of the chapter on Unsaturation runs: "It seems possible that, as the electronic ideas of G. N. Lewis become more generally applied to organic chemistry, we may gain some clearer views on the subject of unsaturated compounds; for his conceptions of firm and looser groupings of electrons seem peculiarly adapted to elucidate many of the problems which have been touched upon in the foregoing pages." Following a brief account of Sugden's work on the parachor is the sentence (Vol. II, p. 24): "It appears that a distinction must be drawn between two kinds of double bonds: the non-polar and the semi-polar." From a perusal of these extracts the average reader would scarcely get the impression that one of the admittedly outstanding achievements of the electronic theory of valency has been its prediction of two types of double bond, and that there are now available three experimental methods for the detection of the presence of the semi-polar bond.

The formula $RN \equiv C$ for *iso*-nitriles, given on p. 27 of Vol. I, has been abandoned for many years.

The chapter on "The Diphenyl Problem" is of a quasi-historical character, and, in addition to a certain looseness of phrasing—"On hydrolysis, this ester yielded a surprise" (p. 314), and a slight ambiguity of formulae (p. 319)—presents the facts in a less striking and less precise manner than has already been done in the Annual Reports of the Chemical Society (1926, 119; 1927, 100; 1928, 114).

Although Professor Stewart deplores the neglect of "the historical branch of organic chemistry" (Vol. I, p. 407), yet a consideration of the development of theoretical organic chemistry since the opening of the present century appears to bring him but little joy—"the subject has yielded very little beyond some minor ideas . . ."; newer subjects have been "drawing the more original minds away from organic problems. The formula of triphenylmethane is certainly a less entrancing subject than, say, the peculiar phenomenon of *iso*-sterism, and it is only natural that inquiring intellects should concentrate themselves by preference upon matters which seem more fundamental than problems of molecular structure" (Vol. I, p. 17). But one joyful note appears—"There is, however, no reason to despair of the future of organic chemistry." "What is urgently needed is a completely new line of development" (Vol. I, p. 17). Is it possible that the author is propounding this in his concluding chapter where reagents are classified as "general" or "specific," or subsequently, after a consideration of the behaviour of hydroxylamine as an oxidising agent, as "synthetical" or "analytical"? (Vol. I, p. 402).

Professor Stewart has collected much useful and interesting information on natural organic compounds, but any book dealing with "Recent Advances" must meet with severe competition while we have the Annual Reports of the Chemical Society as a standard for comparison.

Before the book passes into another edition the elimination of terms such as "parachoric values," "non-iogenic carbon derivatives," might be considered, as well as a loose sentence (Vol. I, p. 254), where it is implied that a synthetic body is both isomeric and identical with trigonelline.

A few misprints in either formulae or text have been noted:—Vol. I, pp. 249, 261, 309, 335; Vol. II, pp. 7, 141, 171.

J. KENYON.

RECENT ADVANCES IN PHYSICAL CHEMISTRY. By S. GLASSTONE, Ph.D., D.Sc. Pp. 470. London: J. A. Churchill. 1931. Price 15s.

There are two reasons why this book will appeal to many readers of THE ANALYST: one is that it is directed more particularly to "chemists who, having started on a professional career . . . find they have neither time nor opportunity to keep in touch with modern developments in physical chemistry" as well as to the student, and the other is that it sets out quite clearly what we do know and have learnt in the past decade, but in such a way as to bring prominently into relief what a lot there is we do not know. Physical chemistry is, perhaps, the most important branch of our science because it deals so much with the fundamentals, the nature and properties of the atom and the molecule; what is valency, why and how do reactions take place, what is solution, and what does catalysis mean?

Dr. Glasstone deals with the atom briefly and clearly; we almost begin to know about it, thanks to Rutherford, Bohr, Aston, Planck and others. The electronic theory of valency, similarly, illuminates a dark place, yet there are so many obscure phenomena here that the theory becomes elaborate—might one say over-elaborate—to meet some of them and others are not met at all. The parachor of Sugden dispels some of our darkness on the structure of compounds and molecules: the parachor is briefly explained as the molecular volume of a compound when its surface tension is unity—an additive property of fundamental import. This much is bright and not too difficult.

Soon after this we plunge into obscurity: the chapters on reactions and catalysis bring out how little we really know of how or why even the simplest reactions take place; the path is strewn with the remains of ingenious theories destroyed by obstinate facts, but there are bright oases (even landmarks) to describe, and real discoveries to chronicle. The theory of even bimolecular reactions is so complex, and in part so uncertain, that one wonders whether there be not yet some unifying principle undiscovered but underlying all reactions; calculations based on vibration, on numbers of collisions, on critical energy, heat of activation, and so on, seem, like the theories of the expanding universe, to be so elaborate as to lose touch with reality, as well as with simplicity.

The chapter on solubility is a welcome change from the complexities of reactions; the internal pressure theory does give practical help, and even guidance, towards the choice of solvents for experimental purposes. The modern dissociation theory, too, is well described (though it is rather mathematical), together with the support it has received from *X*-ray crystallography, so that even if electrolytic theory is not yet complete and free from anomalies, it is at least much more firmly grounded than it was fifteen years ago.

It is obviously impossible to enter here into details or to criticise matters included or omitted; it suffices to say that the book is well written, clear and not too mathematical. It will not be read without an effort by most chemists, but the result of that effort will be a clearer insight into the underlying principles of our science. We are indebted to the author for sifting and pre-digesting a vast amount of complex material and setting before us a well-balanced diet in which the growth-promoting factors are not lacking.

H. E. Cox.

DIZIONARIO DI MERCEOLOGIA E DI CHIMICA APPLICATA. Vol. III, NAFTALINA TO SENA. By Professor G. VITTORIO VILLAVECCHIA AND OTHERS. Fifth edition, revised and enlarged. Milan: Ulrico Hoepli. 1931. Price 60 lire.

The contents of this volume, which follows I and II (reviewed in THE ANALYST for May, 1930) after the lapse of about eighteen months, proceed along the same general lines as the former editions.

Owing to the wide scope of the subjects treated, the information given is necessarily somewhat concise in certain particulars, and in some instances, as in the short article on the thyroid gland under the heading "organotherapeutic agents," is not quite up-to-date. Of special interest are the references to adulterations and alterations to which products are subject, to steps taken to prevent fraud, etc., and the same may be said of the statistical data concerning production, importation, and exportation. As a rule, the last year for which such data are quoted is 1928 or 1929.

As in volumes I and II, a number of new subjects are here considered, and the fact that sections dealing with oysters, sardines, and feathers are found will indicate how extensive a range is covered. The numerous other topics reviewed include naphthalene and its derivatives, nickel, nitrates, essential and other oils, gold, barley, oxygen and oxides, bread, wood pulp, edible pastes, medicinal lozenges and plants, potatoes, hides, pepper, per-salts, pearls, fish, petroleum, precious stones, pills, gunpowder and smokeless powders, metal-cleaning materials, tomatoes, porcelain, perfumery, rhubarb, radium, resins, rice, roses, sands, sago, salt, salicylates, blood, soaps, meerschaum, slags, rye, senna, etc.

Touching the arrangement of the subject matter, it would appear more rational to consider silver nitrate and mercury oxides under the respective headings silver and mercury, instead of giving them separate sections under the titles nitrate of silver and oxides of mercury. The alphabetical index, to appear when the work is completed, should facilitate its use as a dictionary.

As in the two earlier parts, in this, also, the English equivalents are mostly accurate, although a considerable number of obvious English and foreign misprints occur, *e.g.* heat's foot oil, touche stone, quebracko, naphtaline, etc., Geteshead, sintetic, essencs, and so on. "Lachgas" is given as an English name for nitrous oxide (the heading is here protossido di azoto), and "reactives" is found instead of "reagents."

The volume comprises 1044 columns, two on a page. The principal type is good and easily readable, but for statistical matter, etc., a rather small type is employed. Even with our depreciated currency, the price is commendably low.

T. H. POPE.

Publications Received

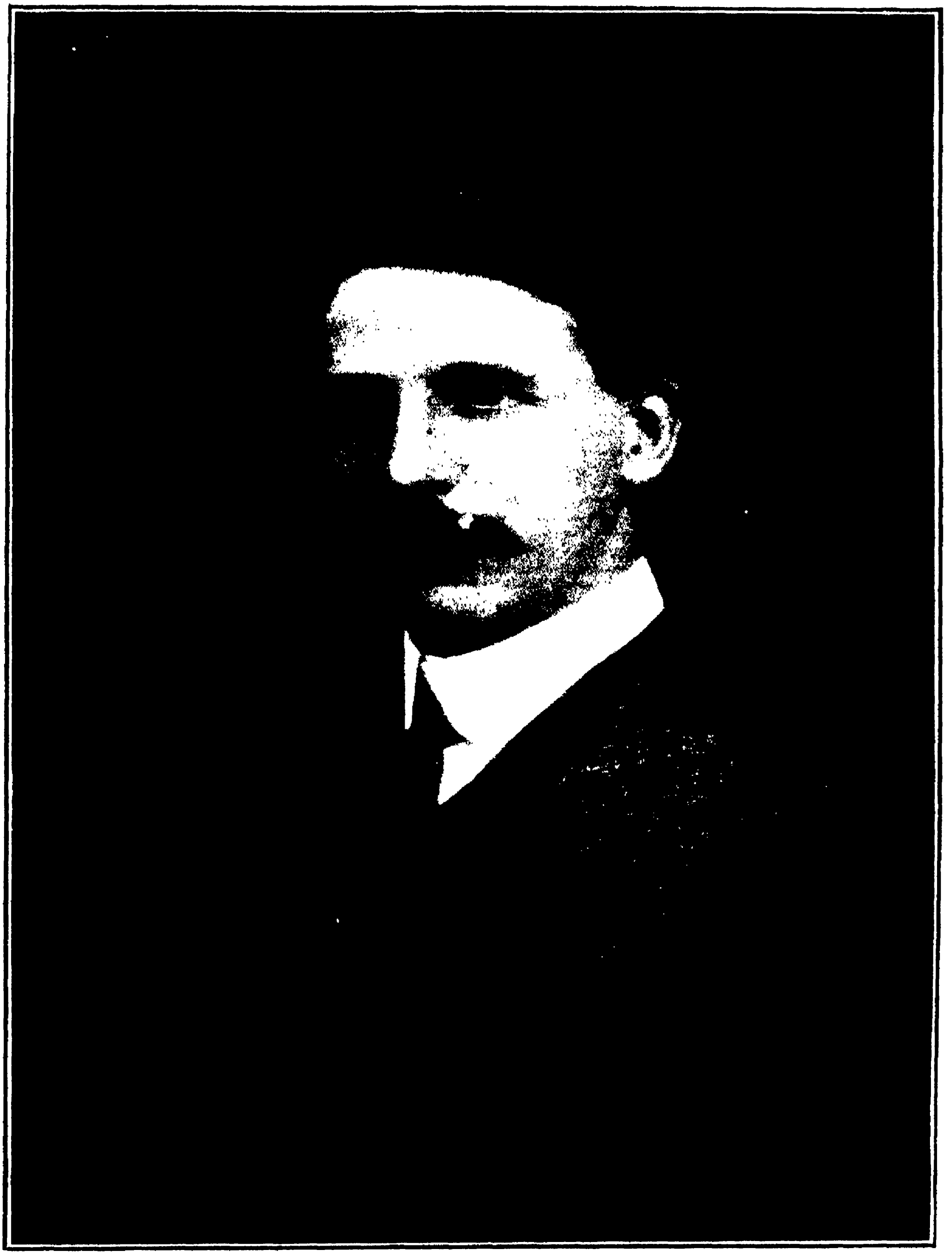
CHEMICAL EMBRYOLOGY. By J. NEEDHAM, M.A., Ph.D. 3 vols. Pp. 2021. Cambridge University Press. 1931. Price 105s. net.

SOIL CONDITIONS AND PLANT GROWTH, Sir E. J. RUSSELL, D.Sc., F.R.S. Sixth Edition. Pp. 636. London: Longmans, Green & Co. 1932. Price 21s. net.

EXAMINATION OF WATER. By W. P. MASON. Sixth Edition. Pp. 224. London: Chapman & Hall. 1931. Price 18s. net.

POTENTIOMETRIC TITRATIONS. By I. M. KOLTHOFF and N. H. FURMAN, Ph.D. Second Edition. Pp. 482. London: Chapman & Hall. 1931. Price 18s. net.

QUANTITATIVE ANALYTISCHE MIKROMETHODEN DER ORGANISCHEN CHEMIE. By C. WEYGAND. Pp. 279. Akademische Verlagges. M.B.H. Leipzig. 1931. Price M.18.



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FEBRUARY, 1932 Vol. LVII., No. 671

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Obituary

WILLIAM FOULKES LOWE

It is with great regret that the death of W. Foulkes Lowe is recorded.

Lowe was an old member of the Society, having been elected in 1888. He served on the Council during the years 1902 and 1903, but his activities in this and in many other ways were restricted by his deafness; yet, the furtherance of the influence of the Society was ever his desire and aim.

Born in 1849 of an old Chester family, he received his education at the King's School, Chester, which then held its classes in the refectory of the Cathedral. He was subsequently a student at the Royal School of Mines, London, and at the Owens College, Manchester, and later became an Associate of the Royal School of Mines and a Fellow of the Institute of Chemistry.

In 1871 he was made a member of the Goldsmiths' Company, and in 1876 was appointed Assayer of the Chester Assay Office, subsequently becoming Assay Master. The Chester Goldsmiths' Company was incorporated in 1700.

To the Society, Lowe was best known as a Public Analyst, and it is of interest to note that he received his first appointment, that of the City of Chester, in 1876. Other appointments as Public Analyst which he held at his death were for the County of Flint (1878), the County of Carnarvon (1881), and the Counties of Anglesey and Denbigh. In addition, he held the position of Official Agricultural Analyst of these counties. A considerable general private practice included the assaying of a large number of gold, lead and zinc ores.

In common with many other Public Analysts, Lowe in his early years lectured, and demonstrated at chemistry lectures (at both Chester and Wrexham) under the old South Kensington Scheme. For many years he was a keen supporter of the Chester Society of Natural Science, Literature and Art, and I well recall some of his early lectures which invariably drew a large audience, no doubt attracted, in part, by the many experiments he would carry out on these occasions. Several years ago the Chester Society awarded him the Kingsley Medal in recognition of his work.

Considering his ability and his extraordinarily wide knowledge, Lowe leaves behind an unexpectedly small amount of published literature. His chief contributions appeared in the *Journal of the Society of Chemical Industry, The Chemical News* and THE ANALYST. His early papers usually referred to the assaying of gold, lead or zinc, but "The Facing of Rice," "Dirt in Milk," "The Occurrence of Copper in Oysters," and "The Adulteration of Spirits of Nitre," are among more recent papers contributed to journals.

Much of his spare time was spent on the water, for he was a keen oarsman, and few had a greater knowledge of sailing. For many years he was a member of the Chester Rowing Club and of the Dee Sailing Club.

He is survived by his widow and three sons, one of whom—Harold Lowe—continues his father's practice, and is a member of our Society, and Public Analyst for Shropshire and elsewhere.

Long will his kindliness live in the hearts of all his colleagues and others who knew him.

F. W. F. ARNAUD.

Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates

XXI. A Reliable Method for the Quantitative Separation of Titanium from Tantalum and Niobium

BY W. R. SCHOELLER, PH.D., AND C. JAHN

(*Work done under the Analytical Investigation Scheme*)

(*Read at the Meeting, November 4th,* 1931)

A PROVISIONAL method for the separation of small amounts of earth acid from titania was described in Section XIV (ANALYST, 1929, 54, 320). Since then we have continued our researches, and have succeeded in elaborating the perfected method recorded below. It is of general applicability to mixtures of earth acid and titania in any proportions; and, as the results obtained by it are reasonably accurate, it brings to a successful conclusion our study (begun by the senior author in 1923) of what was once considered to be a problem of almost insuperable difficulty in mineral analysis.

RATIONALE OF THE METHOD.—It may be recalled that the separation in question has been discussed in three earlier Sections: IX (ANALYST, 1927, **52**, **633**); XIV (*loc. cit.*); and XV (*id.*, 1929, **54**, 453). In each paper a new method for carrying out the separation was indicated: (*A*) Precipitation of the earth acids from the tartrate solution by excess of mineral acid ("tartaric hydrolysis"); (*B*) precipitation of the earth acids by calcium chloride from the oxalate solution containing sodium salicylate ("oxalate salicylate method"); and (*C*) extraction of the bisulphate melt of the mixed oxides with acid tannin solution, the earth acids remaining in the residue ("pyrosulphate tannin method").

We may say at once that continued investigation established the superiority of method *B* over its rivals; hence its principle was made the basis of the new general process. At the same time, the other two methods proved most useful—indeed indispensable—auxiliaries. Method *C* is actually used in our new process for the recovery of the minor earth-acid fraction. As for Method *A*, its great value lies in the specificity of the precipitation reaction as well as in its quantitative applications (*vide* XV, *loc. cit.*, p. 456; XIV, *loc. cit.*, p. 321).

Synopsis.—The first step in the present method (precipitation of the major earth-acid fraction) remains the same as in XIV (*loc. cit.*). Briefly, we produce the calcium oxalate precipitate containing the earth acids, destroy the oxalic acid in the precipitate by means of permanganate in hydrochloric acid solution, and precipitate the earth acids with tannin as heretofore; this furnishes the major fraction P^1. The yellow salicylate filtrate from the oxalate precipitate, however, is now precipitated with tannin and ammonium acetate (*cf.* XVII, ANALYST, 1929, **54**, 709); the ignited precipitate, P^{1a}, represents the titania fraction, which carries a small balance of earth acids. These are recovered from P^{1a} by fusion with bisulphate and application of method *C* as a small precipitate Π^1, which is added to P^1. The sum $(P^1 + P^{1a})$ gives the total amount recovered, $(P^1 + \Pi^1)$ the earth acid recovered.

PRELIMINARY TESTS.—The following results were obtained in a series of exploratory analyses. It should be stated that the earth acids are not precipitated as such with the calcium oxalate, but as bulky salicylic acid complexes, that of tantalum being white, and that of the niobium compound yellow. Exps. 1 and 2, in which no titania was added, show that several mgrms. of earth acid escape precipitation at the P^1 stage:

Exp. 1. Taken, M_2O_5 0·1010 grm. P^1: 0·0972 grm.
„ 2. „ Nb_2O_5 0·1814 „ P^1: 0·1759 „

The table below gives four test separations of niobic oxide and two of tantalic oxide from titania:

Exp.	M_2O_5 taken. Grm.	TiO_2 taken. Grm.	P^1. Grm.	P^{1a}. Grm.	Π^1. Grm.	TiO_2 in $(P^1+\Pi^1)$* Grm.	M_2O_5 in $(P^1+\Pi^1)$† Grm.	M_2O_5 error. Grm.	Total recovery error. Grm.
Nb 3	0·1814	0·0241	0·1805	0·0248	0·0021	0·0026	0·1800	−0·0014	−0·0002
„ 4	0·1814	0·0234	0·1801	0·0234	0·0030	0·0037	0·1794	−0·0020	−0·0013
„ 5	0·2027	0·0246	0·1971	0·0274	0·0038	0·0021	0·1988	−0·0039	−0·0028
„ 6	0·1491	0·0249	0·1476	0·0247	0·0028	0·0019	0·1485	−0·0006	−0·0017
Ta 7	0·1554	0·0122	0·1536	0·0120	0·0015	0·0007	0·1544	−0·0010	−0·0020
„ 8	0·1758	0·0254	0·1779	0·0212	0·0027	0·0049	0·1757	−0·0001	−0·0021

* By colorimetry. † By difference.

The figures prove that 90 per cent. (more or less) of the titania has been eliminated at the cost of a certain loss in earth acid. Re-treatment of $(P^1 + \Pi^1)$ by the same method suggested itself as the means for completing the separation; the products of such re-treatment being P^2, P^{2a}, and Π^2, the titania content of the combined earth-acid fractions $(P^2 + \Pi^2)$ in our final experiments fell below 0·001 grm. Although, therefore, total elimination of the titania from the earth-acid fraction was not achieved, we are quite satisfied with the efficacy of the separation, since all we require is an earth-acid fraction sufficiently low in titania to admit of a satisfactory separation into tantalic and niobic oxides, as specified in Section XI (ANALYST, 1928, 53, 266). The minute amount of residual titania in the pentoxides is, of course, determinable by colorimetry.

Turning our attention to the negative recovery errors observed in the preliminary tests, we located practically the whole of the missing oxides in the filtrate from the tannin precipitate, P^1. This filtrate still contains a fair excess of hydrochloric acid, and, by neutralisation, followed by addition of tannin and excess of ammonium acetate, we obtain a few mgrms. of precipitate, p^1, which is added to P^{1a}.

As a precautionary measure we also re-work the salicylate filtrate from P^{1a}, by simply boiling it down and leaving it overnight. It sometimes yields a fraction of a mgrm. of titania as a small precipitate, p^{1a}, which also is added to P^{1a} before this is worked up for Π^1.

The same manipulations are carried out during the second stage of the separation: the small precipitates, p^2 and p^{2a}, are combined with P^{2a} and converted into Π^2.

The accuracy of the method in its final form does not leave much to be desired, as shown by the results of the test separations (*vide infra*).

PYROSULPHATE TANNIN METHOD FOR SMALL QUANTITIES OF EARTH ACID:—Before describing the improved oxalate salicylate method, we must give certain data on the recovery of the minor earth-acid fraction from the titania fraction (large or small) by means of the pyrosulphate tannin method, which constitutes an important step in the present process.

Procedure.—This is described in XV (*loc. cit.*, p. 455, first paragraph). In this case the precipitate TP, being small, should be left to stand for several hours in the cold (after the liquid containing it has been heated to incipient boiling), prior to filtration, or overnight, if convenient. A 150 c.c. beaker is more suitable than a 400 c.c. one for the quantities involved.

If the proportion of titania in the mixed oxides is high, TP may be re-treated after ignition by the same method, yielding TP^2. The residual titania in TP or TP^2 is determined colorimetrically, M_2O_5 being obtained by difference. (For a specific earth-acid test in TP, see XV, *loc. cit.*, p. 455.)

Results of Test Separations.—The table below shows the results of eight tests on small amounts of mixed pentoxides with increasing additions of titania. Re-treatment of TP was carried out in Exps. 14 to 16; the titania content given in Column 6 was determined colorimetrically in TP or TP^2, the M_2O_5 in Column 7 being taken by difference:

Exp.	M_2O_5. Taken. Grm.	TiO_2. Added. Grm.	TP. Grm.	TP^2. Grm.	TiO_2 in TP. Grm.	M_2O_5 in TP. Grm.	M_2O_5. Error. Grm.
9	0·0061	none	0·0060	—	—	0·0060	−0·0001
10	0·0039	0·0100	0·0041	—	0·0004	0·0037	−0·0002
11	0·0044	0·0200	0·0050	—	0·0008	0·0042	−0·0002
12	0·0046	0·0420	0·0062	—	0·0019	0·0043	−0·0003
13	0·0073	0·0606	0·0092	—	0·0022	0·0070	−0·0003
					in TP^2	in TP^2	
14	0·0055	0·1012	0·0087	0·0052	0·0001	0·0051	−0·0004
15	0·0078	0·1502	0·0149	0·0068	0·0003	0·0065	−0·0013
16	0·0058	0·2034	0·0145	0·0053	0·0003	0·0050	−0·0008

With the exception of the abnormal result in Exp. 15, the recovery of the few mgrms. of earth acid admixed with excess of titania must be considered very satisfactory, especially when it is borne in mind that, until quite recently, even the qualitative recognition of earth acid in such mixtures was very uncertain. The recovery being slightly incomplete, it follows that the negative error increases as the result of the re-treatment of *TP*. For this reason the operator will generally find it preferable, when applying the oxalate salicylate method, to confine himself to a single pyrosulphate tannin treatment of the minor earth-acid fraction; the earth-acid loss will thus be kept at a minimum, while the higher titania content of the fraction is adequately removed in the second salicylate treatment.

Whilst the oxalate salicylate method is the most accurate process for the separation of the earth acids from titania in general, we have in the pyrosulphate tannin method an extremely simple procedure for tracing very small quantities of earth acid in titania.

THE OXALATE SALICYLATE METHOD.—The mixed oxides (about 0·25 grm.) are brought into solution by fusion with potassium bisulphate (3 grms.) in a silica crucible and treatment of the mass with a hot, strong solution of ammonium oxalate (2·0 grms.) in an 800 c.c. beaker. Five grms. of sodium salicylate B.P., dissolved in hot water are added to the boiling solution (bulk, 250 c.c.), which is stirred and precipitated with a slight excess of 20 per cent. calcium chloride solution, added gradually in small portions. The solution must not be allowed to cool; after a few minutes' settling on the water-bath, the supernatant liquid is tested for complete precipitation with a little calcium chloride, and filtered at once by suction on an 11 cm. No. 40 Whatman filter supported by a platinum cone. The precipitate is washed with a hot 2 per cent. sodium salicylate solution until the washings are colourless. The yellow filtrate and washings are transferred to another 800 c.c. beaker and heated to boiling (see *a*).

Major Earth-acid Fraction, P^1.—The oxalate precipitate is returned to the precipitation vessel, the filter being spread against the side of the beaker; the paper is washed with hot water, followed by 40 to 50 c.c. of hydrochloric acid (1:1), and again with water, then ignited, and the ash added to the solution. This is heated and cautiously treated with excess of strong permanganate solution. When the transient brown colour of the higher manganese compounds has been discharged by further boiling (and addition of a few drops of tannin solution if required), the liquid is diluted to 300 c.c. with boiling water, treated with 1 grm. of tannin (fresh, strong solution), boiled for 5 to 10 minutes, and the precipitate P^1 is left to settle for some hours. It is mixed with filter pulp, filtered off under gentle suction, washed with 2 per cent. ammonium chloride solution containing a little tannin, and ignited wet in a porcelain crucible.

Intermediate Fractions p^1, P^{1a}, p^{1a}.—(1) The filtrate from P^1 is neutralised with ammonia (1:1), treated with 5 c.c. of acetic acid and 10 grms. of ammonium acetate, boiled down to 300 c.c., and another 0·5 grm. of tannin added. After settling overnight, the small precipitate, p^1, is collected and washed in the same way as P^1.

(2) The boiling yellow filtrate (*a*) (*supra*) is treated with 10 grms., each, of

ammonium acetate and chloride, and 1 to 2·5 grms. of tannin (about 12 times the weight of the titania) in fresh, strong solution. The voluminous red precipitate is left to settle on the water-bath, and filtered off under gentle suction on a 12·5 cm. filter for quantities up to 0·15 grm.; with larger amounts the precipitate is divided between two filters. After being washed in the same way as P^1, the precipitate P^{1a} is ignited in a silica crucible, together with p^1.

(3) The filtrate and washings from P^{1a} are boiled down to about 250 c.c., 0·5 grm. of tannin being added towards the end, and the liquid left overnight. It is then filtered, and the very small dark precipitate, p^{1a}, washed as before and added to the silica crucible containing P^{1a} and p^1.

Minor Earth-acid Fraction, Π^1.—The ignited intermediate precipitates are fused with potassium bisulphate (1 to 3 grms.), and the cold fusion product is extracted with a 1 per cent. solution of tannin in 5 per cent. sulphuric acid. The hot reagent is poured into the crucible, which is gently heated with a moving bare flame. The contents of the crucible are transferred to a 150 c.c. beaker, and the crucible is rinsed with the reagent (25 to 80 c.c.). The liquid is heated to boiling, then left in the cold for some hours or overnight. The precipitate, Π^1, is collected, washed with 5 per cent. sulphuric acid, ignited, and added to P^1. The filtrate from Π^1, containing the major titania fraction, is reserved if the titania has to be determined.

Re-treatment of ($P^1 + \Pi^1$).—The united precipitates are once more subjected to the whole process so far described. After bisulphate fusion and solution of the product in ammonium oxalate solution, the liquid is filtered if necessary, any residue being ignited and treated with hydrofluoric acid and a drop of sulphuric acid in a small platinum cup; the residue is fused with a speck of bisulphate, taken up with 2 to 3 c.c. of ammonium oxalate solution, and added to the bulk.

The re-treatment yields a major earth-acid fraction, P^2, and the small intermediate fractions p^2, P^{2a}, and p^{2a}; these are combined and worked up by the pyrosulphate tannin method for Π^2, the minor earth-acid fraction, the filtrate from which is combined with that from Π^1. The final products of the operation are: (1) ($P^2+\Pi^2$), which is weighed as $(Ta,Nb)_2O_5$; if bulky, its weight should be checked after lixiviation and another ignition (XIX, ANALYST, 1931, **56**, 309); and (2) the combined filtrate from Π^1 and Π^2.

Determination of Tantalum and Niobium.—The weighed precipitate ($P^2+\Pi^2$) is fused with bisulphate, the mass dissolved in ammonium oxalate solution, and the earth acids separated from each other by Powell and Schoeller's process (IV, ANALYST, 1925, **50**, 489).

Direct Determination of the Titania.—The titania may be taken by difference, the weight of ($P^2 + \Pi^2$) being subtracted from that of the mixed oxides taken. The direct determination may be useful as a check where the quantity of titania is small, though as the titania is a final product, it need not be subjected to further manipulation. For its recovery, we have the choice of two procedures: (1) With smaller amounts of titania, the combined filtrate from Π^1 and Π^2 is diluted, nearly neutralised with ammonia, boiled, and treated with a large excess of ammonium acetate and nitrate. The precipitate is washed with ammonium chloride solution containing a little tannin, ignited, purified by leaching, ignited and weighed; an allowance for iron may have to be made. (2) For large quantities, the combined filtrate is treated for the destruction of the tannin (XIX, *loc. cit.*, 306). The titania in the residual sulphate liquor is determined by thiosulphate hydrolysis.

RESULTS OF TEST SEPARATIONS.—The table below gives the results of a series of six consecutive test separations of mixtures, the composition of which was unknown to the operator. Three contained niobic pentoxide, two tantalic pentoxide, and the last, the mixed pentoxides (see Column 1). In Exps. 17 to 19, pentoxide preponderated over titania; in 20 and 21, titania was the main constituent; in 22, the ratio of pentoxide to titania was about 1:1.

			TiO_2.							
Exp.		M_2O_5. Taken. Grm.	Taken. Grm.	Recovered. Grm.	P^1. Grm.	P^2 leached. Grm.	Π^2. Grm.	$P^2+\Pi^2$. Grm.	M_2O_5. Error. Grm.	TiO_2 in $(P^2+\Pi^2)$. Grm.
Ta	17	0·2023	0·0516	0·0508	0·2036	0·1937	0·0078	0·2015	−0·0008	0·0008
Nb	18	0·2027	0·0513	0·0512	0·2025	0·1954	0·0049	0·2003	−0·0024	0·0006
Nb	19	0·1965	0·0535	0·0531	0·1963	0·1890	0·0053	0·1943	−0·0022	0·00075
Ta	20	0·0335	0·2010	0·1986	0·0314	0·0266	0·0073	0·0339	+0·0004	0·0003
Nb	21	0·0439	0·2067	0·2068	0·0424	0·0368	0·0071	0·0439	0·0000	0·0007
EA	22	0·1257	0·1176	0·1173	0·1273	0·1225	0·0033	0·1258	+0·0001	0·0009

The accuracy of the method will now be considered in the light of the above results. The titania recovery may be dismissed with the remark that it is satisfactory, with the exception of Exp. 20 (error, −0·0024 grm.), in which the recovery of a large quantity was carried out for the first time.

EARTH-ACID RECOVERY.—The experience gained in these investigations makes it increasingly clear that, generally speaking, the precipitation of the earth acids, followed by suitable purification of the precipitates, involves a slight negative error. Usually the loss is negligible, but it is bound to increase with the number of the fractions and with re-precipitation. Exps. 9 to 16 on the pyrosulphate tannin method furnish an example of that tendency. In the oxalate salicylate method, it is counteracted more or less by the slightly incomplete elimination of the titania, of which somewhat less than one mgrm. is found in $(P^2+\Pi^2)$ (last column of table). We feel justified, therefore, in adopting the rule that the net weight of $(P^2+\Pi^2)$, uncorrected for its small titania content, is to be taken as the nearest approach to the true M_2O_5 figure. The M_2O_5 errors in column 8 of the table, which have been computed in accordance with the above rule, prove that we are now able to carry out the separation with a reasonable degree of accuracy without recourse to the correction factors required in the earlier method (the text of pp. 323 and 324, Sect. XIV, is now obsolete). In Exps. 18 and 19, where the error exceeds the usual tolerance, the predominant constituent is tantalum-free niobic oxide, which is a rare case in mineral analysis. Where the M_2O_5 ratio is high, we recommend direct determination of the titania as well as of the earth acids, the total recovery loss being added to M_2O_5, or finally apportioned between the two pentoxides after tannin separation. To sum up, the calculated error in the oxalate salicylate method should not exceed 0·001 grm. (less than 0·5 per cent. on 0·25 grm. of mixed oxides).

Each cycle of operations requires two working days, so that the whole process can be carried out in four days. It is easy of execution, as the successful separation does not depend on delicate adjustments or fractional precipitations.

RETROSPECT.—A few remarks on the principles underlying the separation of titania from the earth acids may conclude this final account of our investigations into the subject.

Differences in chemical behaviour which persist when the elements are in admixture, and hence may serve for their analytical separation, are of two kinds:

(1) *The earth acids do not, whilst titania does, form a soluble salicylic acid complex.* It is upon the formation of the stable crystalloidal salicylic titanium complex (*cf.* preamble to VI, ANALYST, 1926, **51**, 613) that the most efficient separation method is based.

(2) *The earth acids do not, whilst titania does, form a soluble sulphate, nitrate, and chloride.* The earlier attempts (*cf.* XII, ANALYST, 1928, **53**, 470) were based on the inability of tantalum or niobium to form a soluble sulphate, and were defeated by the strong tendency of the reacting elements to form complex hydrolysis precipitates. Tannin counteracts that tendency (XV, *loc. cit.*); hence, when the bisulphate melt is leached with acid tannin solution, titanic sulphate is dissolved, whilst the earth acids remain as insoluble tannin adsorption-complexes.

The connection between the pyrosulphate tannin method and tartaric hydrolysis may not be obvious at first sight, but, nevertheless, the two methods are based on the same difference in chemical deportment: in tartaric hydrolysis the excess of strong mineral acid breaks up the soluble tartaric complexes, with formation of insoluble earth acids and soluble titanium chloride (nitrate). Neither process possesses the accuracy of the oxalate-salicylate method, but both are valuable adjuncts, as shown in this paper and in Section XV (*loc. cit.*).

SUMMARY.—The oxalate-salicylate method for the separation of titania from the earth acids, described in an earlier paper, has now been perfected, with the result that an almost quantitative recovery of the earth acids is achieved, and that less than one mgrm. of titania remains in the final pentoxides. The process is claimed to be accurate within 0·5 per cent. The application of the pyrosulphate tannin method to the determination of small amounts of earth acid in titania is explained. The principles underlying the separation of titania from the earth acids are briefly discussed.

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DISCUSSION

Dr. B. S. EVANS said that he would like to preface his remarks with congratulations to Dr. Schoeller on his remarkable results, not only in the present paper, but also in others of the same series. He (the speaker) had repeatedly found them indispensable when dealing with niobium and tantalum. He would like to raise one point regarding the relatively bad result put down for niobium in the separation of niobium from titanium. Would the process be safe where one got, not pure niobium, but a mixture of niobium and tantalum: that was to say, was the error, which he noticed was repeated, bound up with the absence of tantalum, and would it be put right by its presence? If so, could Dr. Schoeller give any indication of the amount of tantalum which would make it safe?

Dr. SCHOELLER, in reply, said that the recovery of the niobium appeared to be improved by the presence of tantalum, as in the last experiment shown in the Table, in which a mixture of tantalic and niobic oxides (61·4 per cent. Ta_2O_5) was used and a satisfactory result was obtained. He and Mr. Jahn had not, however, so far, been able to carry out enough work to state the minimum amount of tantalic oxide which would correct the niobium recovery.

The Determination of Chlorides in Dairy Products and Biological Material

By W. L. DAVIES, M.Sc., Ph.D., F.I.C.

(*Read at the Meeting, October 7th,* 1931.)

The comparative ease and accuracy with which chloride can be determined suggest the application of the determinations as checks on other operations, such as control of sampling, checking of repeated samplings, and the evaluation of the volume of a precipitate. The salt content of food refuse of a variable composition, *e.g.* fish meal or hotel refuse, is of importance in the feeding of animals.

The Dry-ashing Method of Chloride Estimation.—Incineration of the material, followed by a determination of the chloride in the ash, has many disadvantages, such as tendency to loss of chloride by direct volatilisation and loss of hydrochloric acid by the action of non-volatile acid oxides on chlorides. A determination by this method requires a considerable amount of time, especially when fluids have to be evaporated. The alkali chlorides are volatile at red heat,[1] and blank determinations are necessary when alkaline earth oxides are added to "fix" the chlorides.

Wet Methods of Determining Chloride.—The chlorides in biological material are present as easily soluble salts, and the problem of a wet determination centres around the quantitative solution in a medium which will not interfere with the Volhard method. All colloidal material likely to react with silver salts, either by adsorption or base exchange, must be broken down, and the resulting colour of the solution must be such that the end-point in the titration can be accurately detected. The interference of other salts, such as phosphates, silicates and carbonates, can be overcome by using the Volhard method of titration exclusively. The direct titration of chloride in butter, for instance, is to be deprecated, owing to the curd absorbing silver ions.

The most convenient method of destroying organic matter is by digestion with dilute nitric acid. This has been applied by Van Slyke[2] to the determination of chlorides in blood, in place of the ashing process advised by Whitehorn.[3] The method, applied to dry material, consists in wetting the sample thoroughly with water, warming, if necessary, then adding standard silver nitrate solution in excess of the equivalent of chloride present, pure concentrated nitric acid to make the concentration about 25 per cent., and boiling the contents of the flask over gauze. In the Carius method of determining chlorine in organic compounds, even fuming nitric acid has no effect on silver chloride, since, in the presence of silver salts, the solubility of silver chloride is of a much lower order of magnitude than is likely to interfere with the accuracy of the method. The disintegration effected by nitric acid needs only to reach the stage when all possibly interfering substances, such as proteins and complex carbohydrates, are broken down to true water-soluble compounds, to make complete wet-ashing unnecessary. Globules of free fat do not interfere with the subsequent titration and need not be removed. When removal of silver chloride, owing to its bulk, is necessary, the fat globules are also removed.

IMPROVEMENT OF THE COLOUR OF THE SOLUTION AND THE END-POINT.—With all material containing protein the liquid after digestion possesses a lemon-yellow to yellowish-brown colour, due to the nitration of aromatic amino-acids. Dilution of the liquid usually also dilutes the colour sufficiently to remove any difficulty in observing a sharp end-point. The elimination of nitrous acid cannot, of course, be effected by boiling the concentrated digest, and since boiling the diluted solution would unnecessarily prolong the determination, the addition of urea in slight excess is efficacious in decolorising the hot solution. This does not completely destroy the yellow colour, but it prevents the usual deepening of the colour experienced on adding iron alum solution.

The addition of urea thus removes difficulties connected with the end-point, and the addition of acetone, in amount sufficient to give a final concentration of 5 per cent., gives a still sharper end-point. In the Volhard method it is advisable to filter off the silver chloride, owing to the reaction between it and ferric thiocyanate.[4] With large amounts of silver chloride, and in the presence of much fibre, sand, and undecomposed fat, this is advantageous, in that it allows the final titration to be carried out in a liquid containing the minimum amount of suspended material, and that in strong sunlight the silver chloride darkens considerably. But with small amounts of silver chloride, and on titrating immediately and quickly after dilution, no advantage is gained by removing the precipitate. Acetone has a protective effect in preserving the colour of ferric thiocyanate, even in the presence of appreciable amounts of pyrophosphate, possibly owing to a combined solvent and oxidation effect (due to the peroxide present).

DESCRIPTION OF THE METHOD.—The wet method for chloride determination may be described as follows:

(*a*) *Milk* (*and Biological or other Fluids*).—Ten ml. of milk, if the result is required as mgrms. of chlorine per 100 ml., or 10 ml. weighed, if the percentage of chlorine or sodium chloride is required, are pipetted into a 250 ml. flask, and 10 ml. of 0·05 *N* silver nitrate solution are mixed with it. Two ml. of saturated potassium permanganate solution (approx. 6 per cent.), and 10 ml. of pure concentrated nitric acid are added, and the contents of the flask are boiled over gauze in a draught chamber until the liquid is clear (except for the small amount of precipitate) and reddish-brown fumes are copiously evolved (three to four minutes). Under similar conditions the volume of nitrous fumes varies directly with the lactose content of milk, and milk of low chlorine content (see below) and correspondingly high lactose content yields fumes more quickly and copiously than milk of low lactose or high chlorine content. A pinch of urea (0·25 grm.) is added to the hot solution, and the contents of the flask are diluted to about 100 ml. Six ml. of acetone and 1 ml. of a saturated solution of iron alum in 10 per cent.

nitric acid (prepared by boiling excess of iron alum in 10 per cent. nitric acid, cooling and filtering) are added, and the excess of silver nitrate is titrated with 0·05 *N* potassium thiocyanate (standardised upon the above-mentioned silver nitrate by means of standard potassium chloride solution). A blank determination for reagents is also made when standardising the silver nitrate. (Without exception, the above reagents have been found absolutely free from chlorides, provided *pure* nitric acid was used. Even commercial iron alum is free from chloride, but fresh samples should be tested.)

The above quantities are suitable for most samples of milk, and 10 ml. of 0·05 *N* silver nitrate solution are equivalent to 177·2 mgrms. of chlorine per 100 ml. when working with 10 ml. of milk. Some samples give a result exceeding this value, and this necessitates the addition of 15 or 20 ml. of silver nitrate before digestion. The determination takes very little time, and thirty samples can easily be dealt with in an hour. All biological and other fluids can be treated in the same way. Urine does not require boiling with acid, and the Volhard method can be used in the cold, but the silver chloride, owing to its bulk, must be filtered off.

(*b*) *Solid Material.*—A sufficient weight of material to contain 0·15 to 0·30 grm. of chlorine (combined) is weighed into a 250 ml. conical flask, and well wetted or soaked with water, warming if necessary, and 25 ml. of 0·05 *N* silver nitrate solution are added. After thorough shaking, 10 ml. of saturated permanganate solution and 25 ml. of concentrated nitric acid are added, and the contents of the flask are boiled over gauze. Starchy food disintegrates quickly, yielding a yellow solution, but foods rich in protein, especially those containing fibrous protein (*e.g.* fish meal), take longer to dissolve. If the amount of salt is considerable, or if there is a large volume of unattacked fibrous material, fat or sand, the cooled, diluted (100 ml.) digest is filtered by suction, the precipitate being washed repeatedly with hot 5 per cent. nitric acid. But when the amount of solid material is small, the excess of silver nitrate may be determined at once. The filtrate is made up to standard volume (200 ml.), and the excess of silver nitrate is determined in aliquot portions (or on the whole liquid) by titrating with 0·05 *N* thiocyanate solution, using 1 ml. of saturated iron alum as indicator, after adding acetone until the solution contains 5 per cent. In determinations in which excess of silver nitrate was not added at the outset, it is necessary to repeat the determination on a fresh amount of material; further addition of silver nitrate after acid digestion is useless.

Examples of Results.—A few examples of triplicate determinations on some common foodstuffs are given in Table I.

Table I.

Silver chloride not filtered off, unless stated.

(*a*) *Milk.* A. 89·4; 89·5; 89·5 mgrms. Cl per 100 ml.
B. 110·2; 110·2; 110·3 ,, ,, ,, ,, ,,

(Samples of milk may be encountered containing from 60 to over 300 mgrms. of chlorine per 100 ml. The average range is from 70 to 130 mgrms.)

TABLE 1.—*continued.*

		Sodium Chloride. Per cent.		
(b) Other Dairy Products.				
Cheese.	New Zealand Cheddar	1·62;	1·65;	1·63
	English Cheddar	1·56;	1·58;	1·56
Butter.	New Zealand, salted	1·61;	1·62;	1·62
	High salt, experimental	6·13;	6·12;	6·14
Dried milk		1·99;	2·00;	2·00
Dry whey and separated milk		2·19;	2·18;	2·19
(c) Other Foodstuffs.				
Bread (white crumb)		0·956;	0·958;	0·955
Biscuit (broken)		0·110;	0·111;	0·112
*Prepared meat (paste)		3·68;	3·67;	3·68
Dried yeast		nil;	nil	
*Fish meal	(1)	1·97;	1·96;	1·95
	(2)	2·56;	2·57;	2·55

* Silver chloride filtered off.

THE VALUE OF A QUICK METHOD FOR CHLORINE DETERMINATION AS APPLIED TO OTHER OPERATIONS.—(1) SAMPLING.—The ease with which the determination can be carried out commends it as a rapid means of checking the accuracy of sampling or of checking replicated samples. It can also serve as a check on the equalisation of material in bulk and on thorough mixing, *e.g.* of milk.

Table II illustrates the application of the chloride content of milk as a test for the equalisation of the bulk milk of a large herd of cows. (This work was done during the study of a herd giving low solids-not-fat consistently; hence the low solids-not-fat figures. The examples given show the importance of equalising such milk.)

TABLE II.

Chlorine (chloride) as mgrms. per 100 ml. and percentage of solids-not-fat.

			Churn No.					
			1.	2.	3.	4.	5.	6.
1.	8/4/30 a.m.	Chlorine	113	122	137	122	122	—
		Solids-not-fat	8·31	8·38	7·85	8·47	8·43	—
2.	8/4/30 p.m.	Chlorine	117	117	127	121	—	—
		Solids-not-fat	8·38	8·50	8·39	8·42	—	—
3.	9/4/30 a.m.	Chlorine	114	119	116	111	129	144
		Solids-not-fat	8·49	8·45	8·52	8·56	8·01	7·77
4.	9/4/30 p.m.	Chlorine	118	118	119	115	—	—
		Solids-not-fat	8·30	8·30	8·44	8·45	—	—
5.	10/4/30 a.m.	Chlorine	123	122	123	123	123	145
		Solids-not-fat	8·34	8·51	8·48	8·46	8·41	7·73
6.	11/4/30 a.m.	Chlorine	118	107	112	115	120	132
		Solids-not-fat	8·34	8·48	8·52	8·44	8·54	8·01

Examples 2 and 4 show well-equalised milk. Churn 3 in Ex. 1, Churns 5 and 6 in Ex. 3, and Churn 6 in Ex. 5 and 6, show high chloride figures and low solids-not-fat content, owing to inefficient equalising.

(2) EVALUATION OF THE VOLUME OF A PRECIPITATE.—Occasionally the volume of the precipitate obtained while preparing a clear serum has to be taken into account. To obtain the copper serum of milk, 100 ml. were added to 25 ml. of copper sulphate (containing 72·5 grms. per litre), and, after shaking and leaving for five minutes, the clear serum was filtered off. On determining the chloride in the milk and serum, the volume of the precipitate was calculated:

Chloride content of milk = 113·8 mgrms. Cl per 100 ml.
,, ,, ,, copper serum = 94·4 mgrms. ,, ,, ,, ,,
or 118·0 mgrms. ,, ,, 125 ,,

$$\text{Volume of serum} = \frac{113{\cdot}8}{118{\cdot}0} \times 125 = 120{\cdot}6 \text{ ml.}$$

Hence the volume of precipitate = 125 − 120·6 = 4·4 ml.

(Woodman[5] cites 2·6 ml. as the volume of precipitate from 65 ml. of milk, or 4·0 ml. for 100 c.c. This value, of course, varies with the fat content of the sample.)

(3) CALCULATION OF THE APPROXIMATE LACTOSE CONTENT OF MILK.—The complementary relationship between lactose and chlorides in milk has evoked much discussion, and various values and constants have been suggested. Of these, "the simplified molecular constant" (S.M.C.), suggested by Matthieu and Ferré[6] (critically reviewed by Porcher[7]), is the most useful. Chlorides and lactose account for 75 per cent. of the osmotic pressure of genuine fresh normal milk, irrespective of the composition of the sample, and it is suggested that a lowering of lactose content is accompanied by an isotonic increase in chloride content, and that one grm. of common salt is equivalent in this respect to 11·9 grms. of lactose. The S.M.C. is the lactose equivalent of the common salt, plus lactose of milk in grms. per litre [or lactose (grms. per litre) plus 11·9 × NaCl (grms. per litre)], and is roughly equivalent to 70. On a percentage basis, therefore:

Per cent. of lactose + 11·9 × per cent. of sodium chloride = 7 (approximately) or
Per cent. of lactose + 19·6 × per cent. of chlorine = 7.

For a very large number of samples analysed by various workers the S.M.C. has been found to vary from 69 to 73, with a few samples outside this range. Calculation of the constant on a fat-free serum basis gives more comparable results. The constant is claimed to show a distinction between watered milks (S.M.C. falling to 65 with 5 to 10 per cent. of added water) and samples low in solids-not-fat (normal values of the S.M.C.).

From the above equations, the chloride content being known, the lactose figure can be deduced approximately. A few results are given in Table III.

TABLE III.

Sample.	1.	2.	3.	4.	5.	6.	7.
Chlorine, per cent. ..	0·075	0·086	0·100	0·168	0·169	0·178	0·188
Lactose (calc.), per cent.	5·53	5·31	5·00	3·71	3·69	3·51	3·31
Lactose (determined by copper reduction method)	5·50	5·27	5·01	3·74	3·79	3·42	3·33
S.M.C. (from lactose found)	69·3	69·6	70·5	70·3	70·9	69·1	70·2

Samples 1 to 3 were normal in composition, whilst samples 4 to 7 were low in solids-not-fat, the deficient constituent being lactose.

KOESTLER NUMBER.—Koestler,[8] studying the milk of cows when drying off, observed a rapid rise in chloride content, and, taking into account the inter-relationship between lactose and chloride content, suggested that abnormal milk was being secreted when the value $\frac{100 \times \text{Cl per cent.}}{\text{lactose per cent.}}$ exceeded 3·5 (the Koestler number). From the chloride content and the S.M.C. relationship, the value can be calculated from the expression $\frac{100 \times \text{Cl per cent.}}{7 - (19{\cdot}6 \times \text{Cl per cent.})}$. Equating this to 3·5 (as the maximum for normal milk), the chlorine content becomes 0·146 per cent., *i.e.* all samples containing over 0·146 per cent. of chlorine are abnormal. Most milk samples show a range in Koestler number of 1 to 3, corresponding with a chloride (Cl) content of from 0·070 to 0·130 per cent.

By calculating the approximate lactose content from the chlorine figure it can be deduced whether deficiency in solids-not-fat is caused by lactose or not. This can quickly be done by the rough rule that for every 0·050 per cent. of chlorine (more accurately, 0·051 grm. of chlorine per 100 ml.) the lactose content is lowered 1 per cent. from a hypothetical maximum of 7 per cent. (*e.g.* in a sample of milk containing 0·125 per cent. of chlorine, the lactose is, roughly,

$$7 - \frac{125}{50} = 4{\cdot}5 \text{ per cent.}).$$

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DISCUSSION.

Mr. E. HINKS asked, regarding the determination of chlorine, what proof the author had that the chlorine figure he obtained was the right one. The deductions drawn from the chlorine content were extremely interesting, especially those referring to the volume of precipitate. The Milk Products Sub-Committee, when considering this, tried the chloride content as a "tell-tale" and failed, since they could not get the chloride determination sufficiently accurate, and they had to adopt other methods. He was not sure how the chloride method would work out for condensed milk. It was extraordinary that variations from 60 to 300 mgrms. of chlorine per 100 c.c. could be encountered, and surely the samples showing high values were abnormal.

Mr. BACHARACH referred to the chloride content of dried milk, given as 2 per cent. If this represented eight times the concentration of the original milk, it would mean that the chloride concentration was 0·250 per cent. in the milk, which was decidedly abnormal.

Mr. **Strafford** asked if Dr. Davies had ever tried the electrometric method. This saved a great deal of time, and the outlay for plant was not very great.

Dr. W. L. **Davies** replied that he had tested the method by adding definite amounts of potassium chloride, and that quantitative recovery had been obtained. The volume of precipitate had also been tested half-a-dozen times with different chloride contents. The data collected for illustrating the variation of chloride content in milk arose from other researches, and the extraordinary variations of from 60 to 300 mgrms. of chlorine per 100 c.c., quoted, were obtained from the study of individual samples of milk from a herd giving low solids-not-fat figures. Such a variation would be rare in a normal herd. The chloride content of dried milk was given as per cent. of sodium chloride, which would give a normal chlorine figure if reported as chlorine per cent. With regard to electrometric methods, the conductivity method was successful, but a potentiometric method would involve clearing the solution of protein, owing to adsorptive effects.

Addendum.—The end-point of the titration of excess silver nitrate in the determination of chlorides in milk is sensitive to the nearest drop, and this, with the strengths of solutions used, justifies the calculation of the chloride content only to the nearest 0·5 mgrm. per 100 ml. milk. For quick work on a large number of samples it is satisfactory, for most purposes, to determine the chloride to the nearest mgrm. per 100 ml., *i.e.*, the percentage of chloride is accurate to the third decimal place. For the same reason the limitations of the fineness of the end-point in using the method for the calculation of the volume of precipitate justify its being given only to within the limits of ±0·25 ml. in accuracy.

Oil from Malayan *Aleurites Montana* and the Properties of Hong Kong Oil

By T. HEDLEY BARRY

(*Read at the Meeting, December 2nd,* 1931)

In September, 1930, I received from the Director of Agriculture, Federated Malay Straits and Straits Settlements, a 5-lb. sample of kernels collected from *Aleurites montana* trees growing at the Experimental Station, Serdang, which were planted during March, 1925. The seeds from which these trees were grown were obtained from the Botanical and Forestry Department, Hong Kong. The fruits were collected on August 8th, 1930, and the kernels were air-dried for ten days before despatch.

From the economic point of view the experiments in Malaya have not been satisfactory so far, and the authorities have come to the conclusion that *Aleurites montana* is not suited for cultivation in the plains of Malaya.

A description of the growth and condition of the trees up to the end of 1928 was published by J. N. Milsum and T. D. Marsh (*Malayan Agric. J.*, 1929, No. 2, p. 47).

Although the ultimate result of the experiments was not entirely satisfactory, the trees made rapid growth during the early stages, and the results of an examination of the oil extracted from the kernels collected in 1928 from three-year-old trees were published by C. D. V. Georgi and G. L. Teik (*Malayan Agric. J.*, 1928, No. 8, p. 296).

Apart from the purely scientific interest attaching to these experiments, the examination of oil from *Aleurites montana* is of practical importance. It is known that the oil from S. China, which is generally sold under the name "Hong Kong" oil, is derived from two species of *Aleurites*—*A. Fordii*, Hemsl, and *A. montana* (Lour), Wilson.

According to E. H. Wilson (*Bull. Imp. Inst.*, 1913, **11**, 441), the bulk of the oil exported is obtained from *A. Fordii*. Recently an important paper has been published by F. A. McClure (*Lingnan Sci. J.*, 1930, **9**, 233), giving an account of his tour of the Provinces of Kwangtung, Kiangsi, Anhwei, Kiangsu and Hupeh, which covered some of the most important areas in which the tung oil tree is cultivated.

According to McClure the cultivation of *A. montana* is confined largely to the provinces of Kwangtung and Kiangsi. Oil from this species is, therefore, to be expected in the commercial article exported from Canton or Hong Kong.

It has long been recognised in the trade that Hong Kong wood oil is of different quality from that generally known as Hankow oil. The difference is doubtless mainly due to the greater care in extraction and purification exercised at Hankow, where the Americans, in particular, have established trading centres.

At the same time the fact that Hong Kong oil is admittedly derived from two species of trees suggests the possibility that the oil from *A. montana* is not absolutely identical with that from *A. Fordii*. The oil examined by Georgi had the following characteristics:—Sp. gr., 0·939; acid value, 3·6; saponification value, 195·5; iodine value (Wijs), 160·3; unsaponifiable matter, 0·6 per cent.; refractive index at 20° C., 1·5098. The most notable feature in these results is the low refractive index. The figure, however, was confirmed by the Department of Agriculture, F.M.S. and S.S., the refractive index being kindly re-determined at my request on the 29th October, 1930, and found to be 1·5097 at 20° C., which is practically the same as the published figure. The most obvious explanation of this abnormally low refractive index would appear to be that the trees were not developing normally, with the result that the oil was of a somewhat different composition from that of the normal product.

Oils obtained from *A. Fordii*, grown in China and in Kenya, have been examined, and the results are summarised in the *Bull. Imp. Inst.*, 1930, **28**, 268, and in no case is a refractive index lower than 1·518 at 20° C. recorded. The lowest recorded refractive index for an authentic *A. Fordii* oil, so far as I am aware, is 1·5155 for a Californian cold-pressed oil (David Fairchild, Circ. 108, *Bull. Plant. Ind.*, Washington, 1913), but this was considered an unusual sample, the seed having been stored for over a year. The few samples of oils from *A. montana* which have been reported show a considerable variation in this respect.

Aleurites montana.	Refractive index at 20° C.
Burma[1]	1·4755
Japan[2]	1·5221
China, 1929[3]	1·5134
1930	1·5164
Malaya[4]	1·5098

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[1] *Indian Forest Records*, 1923, **10**, Pt. 2, p. 11.

[2] *Trav. Lab. Mat. Med.*, Paris, 1926, **17**, 24.

[3] *Bull. Imp. Inst.*, 1930, **28**, No. 3, p. 270.

[4] *Malayan Agric. J.*, 1928, **16**, 296.

Aleurites Fordii.	Refractive index at 20° C.
China (*a*)	1·5229
(*b*)	1·5204
Kenya	1·5194

(*Bull. Imp. Inst.*, 1930, **28**, No. 3, p. 268.)

The oil from the present sample was, therefore, examined, with particular reference to these points, and also to the possibility of this apparent difference between the two oils having some bearing upon the difference between the commercial oils from Hong Kong and Hankow.

EXPERIMENTAL.—The oil was extracted from the beans both by pressure and by cold extraction with petroleum spirit (b. pt. 40° to 60° C.).

Extraction by pressure was effected in a small hand-press, giving about 1½ tons per square inch. By the first method 42 per cent. and by the second 19·2 per cent. of oil were obtained. The total oil-content was determined by extraction with boiling petroleum spirit (Georgi and Teik found 43·2 per cent.). The meal from the hand-press was extracted with cold petroleum spirit.

The oil extracted with petroleum spirit both from the pressed meal and from the original beans proved very retentive of the solvent, and isomerised much more rapidly than did the cold-pressed oil. Even when kept in the dark, it set almost solid in the course of a few weeks, whilst that obtained by pressure remained perfectly clear and liquid when kept in a plain bottle, although, of course, not exposed to the direct action of light.

In order to remove the last traces of solvent from the extracted oil, it was necessary to pass steam through it for some minutes. After this treatment the oil was dried and filtered.

REFRACTIVE INDEX.—The following results were obtained on the various samples:

		Refractive index at 20° C.
(1)	Solvent-extracted, (*a*) before steaming	1·5086
	(*b*) after steaming	1·5128
(2)	Cold-pressed	1·5135
(3)	Solvent-extracted from pressed cake and steamed to remove solvent	1·5125

For comparative purposes, the following results were obtained with samples of Chinese oils, from *A. Fordii* and *A. montana*, and from American *A. Fordii* :—

		Refractive index at 20° C.
(1)	Chinese *Aleurites montana*	1·5160
(2)	Chinese *A. Fordii*	1·5190
(3)	American tung oil, Corporation Standard	1·5190

The sample of Chinese *montana* oil was crushed by a firm in Hull from seeds obtained from China, and I am indebted to Dr. L. A. Jordan, Director of the Research Association of British Paint, Colour and Varnish Manufacturers, for the sample.

As regards the Browne Test, it is evident that all the samples of *montana* oil reported polymerise much more slowly than oils from *A. Fordii* (*Bull. Imp. Inst.*, 1930, **28**, 268).

Aleurites montana.		Browne test. Minutes.
China	(*a*)	24·0
	(*b*)	20·5
Burma		16·0

For the oils extracted from the Malayan kernels the results were:

	Minutes.
Cold-pressed oil	15¾
Solvent-extracted	18½

Parallel tests with Chinese and American oils gave:

	Minutes.
Chinese *A. montana*—hot-pressed	11¾
Chinese *A. Fordii*	9¾
American *A. Fordii*	9¼

IODINE VALUE.—The iodine value was determined by the method of Wijs (1 hour at 22° C.), and the thiocyanogen value by Kaufmann's method (*Ber.*, 1929, **62**, 392; ANALYST, 1929, **54**, 304), the following results being obtained:

	Wijs' method.	Kaufmann's method.
Malayan *A. montana*—		
(*a*) Cold-pressed	163	81·1
(*b*) Solvent-extracted from pressed meal	160	78·6
(*c*) Solvent extracted from beans	—	81·4
Chinese *A. montana*	—	81·3
American *A. Fordii*	166	82·7

From the above results it appears that the oil from *A. montana* has a consistently lower refractive index than oil from *A. Fordii*, and that trees growing in unsuitable districts may yield an oil of even lower refractive index than the normal Chinese *A. montana*. It should, however, be borne in mind that the number of samples of authenticated botanical origin which have been examined is still too small to justify dogmatic assertion on this point.

As regards refractive index, the lower limit generally accepted, in both Europe and America, is 1·518 at 20° C., and, therefore, none of the samples of *montana* oil from the kernels referred to in this paper would pass the specification.

Regarding polymerisation, apart from the Chinese *montana* oil, which just falls within the specified limit (12 minutes), all the *montana* oils take considerably longer than *Fordii* oils. In this connection it is of importance to note that the consistence of the jelly is equally, if not more, important than the time of setting. In the case of these *montana* oils, it was noted that the jelly, though distinctly softer than that from Hankow oils or from *A. Fordii*, was not sticky, and its general condition was much firmer than that which is obtained from Hankow or *Fordii* oils adulterated to give a setting time of the same order as *montana* oil.

As to the bearing of these results on the properties of Hong Kong oil, as distinct from Hankow oil, one would expect that the presence of *A. montana* oil would reduce the refractive index and increase the polymerisation time. The oil from *A. montana* may be more liable to variation than that from *A. Fordii*, and much more information is necessary before the limits of variation in its analytical constants can be fixed.

In this connection, however, a recent report by A. R. Penfold and F. R. Morrison (*Bull.* 12, Technological Museum, Sydney) on a series of Australian-grown *A. Fordii* is of interest as indicating that the oil from *A. Fordii* also varies considerably in properties according to the condition of the tree. The refractive indices of the samples examined by these workers vary widely, and the oils obtained by solvent-extraction in several cases show a lower refractive index than corresponding samples obtained by pressure, *e.g.* the oil (25 per cent.) extracted by pressure had the refractive index (25° C.) 1·5152, whilst the oil (52 per cent.) solvent-extracted had the refractive index 1·5133. Some of the solvent-extracted oils also appear to have isomerised very rapidly.

HONG KONG OIL.—It is well known that varnish makers differ in their opinion as to the value of "Hong Kong Oil," some refusing to use it, whereas others apparently find no difficulty in making satisfactory products with it. Varnish-making, however, is so complicated and varied a process, and the personal factor plays so large a part in determining the results, that it is impossible to say how far the objections to Hong Kong oil are due to prejudice and local usage or to physical characteristics, such as colour and freedom from "foots," which could be remedied by improved methods of extraction and refining, or whether there is a fundamental difference in composition which has an effect on the resulting varnish.

Satisfactory varnish can undoubtedly be made from Hong Kong oil. Considerable quantities of the oil are used both in this country and on the continent, although, normally, Hong Kong oil fetches a somewhat lower price than Hankow oil.

As to the analytical constants of Hong Kong as distinct from Hankow oil, little has been published. China wood oil, shipped through Hong Kong, is examined by the Government Laboratory, and I am much indebted to Mr. E. R. Dovey, the Government Analyst, for his cordial assistance in giving information as to the work in Hong Kong. The specification of the "Association of Exporters and Dealers of Hong Kong" for South China wood oil is as follows:

"Specific gravity	not less than 0·9400 at 15° C.
Refractive index	,, ,, ,, 1·5184 at 20° C.
Total impurities (dirt, moisture, etc.) ..	less than 1 per cent.

In addition, the oil shall pass an accepted polymerisation test—either Worstall, Browne, Bacon or Chapman."

The Browne Test, the originator of which was formerly Government Analyst at Hong Kong, is used in the Hong Kong Laboratory. In the case of 80 per cent. of the oil passing through Hong Kong, samples are taken by Government analysts, but as regards the rest, a sample is frequently sent to the laboratory, in which case, of course, no guarantee as to the authenticity of the sample can be given.

It is rather remarkable to note that, although Hong Kong oil is considered inferior, and the authenticated oils from *A. montana*, so far examined, show the peculiarities of comparatively low refractive index and slow polymerisation, the specification drawn up by the Hong Kong Laboratory, which deals particularly with oil from the districts in which *A. montana* grows, actually sets a higher standard in the matter of refractive index than do either European or American laboratories for "Hankow oil," which is considered to be the purer grade and consists essentially of oil from *A. Fordii*.

McClure was able to establish the fact that the Chinese in the regions he visited were well acquainted with the distinction between the two trees. The name "T'ung Yau Shue" is applied to both *A. montana* and *A. Fordii*, but where both species grow together distinctive names are used.

In Kiangtung, *A. montana* is known as "Ten Thousand Year Tung"—"Maan Nin T'ung," and *A. Fordii* as the "Three Year Tung"—"Saam Nin T'ung" or the "Early Rice Tung"—"Tso Woh T'ung," the *A. Fordii* maturing more rapidly in South China than the *A. montana*, though, apparently, it is not so long lived.

In Anhwei, however, the name "Maan Nin T'ung" is said to indicate trees which bear fruit in three years, but in this province only *A. Fordii* appears to be cultivated. Deliberate adulteration of the oil by the native pressers was formerly common, but all the Chinese buyers are now equipped with refractometers, and, consequently, adulteration in that quarter, at least, has practically ceased, though, as the natives use the same press for all oil seeds, the presence of small amounts of other oils is inevitable, and of these, cottonseed oil is said by a Hankow authority to be the most common.

A recent report on the Economic Condition of China (*Dept. Overseas Trade*, Aug. 1930), however, rather tends to destroy confidence in this statement. Apparently, modern factories are now established at Chingking, Changtuh and Wanhsien, where the oil is refined and shipped in bulk by way of Hankow.

Some 8000 tons were shipped in this way in 1929, and the amount is increasing. It is stated, however, that there has been a notable fall in the quality of the Chinese oil, and that the practice of adulteration, which was formerly common at the collecting centres, is now practised to an increasing extent by the natives themselves in the inland districts.

I have had occasion to examine a number of Hong Kong oils which had been shipped to this country during 1930, and, with the exception of one batch of about ten tons (concerning which an unsuccessful claim for adulteration was made), had been absorbed by the paint and varnish trade in Europe without complaint.

The result of the examination of 23 samples may be summarised as follows:

	Maximum.	Minimum.	Average.
Acid value	11·27	3·23	7·04
Refractive index at 20° C. ..	1·5172	1·5153	1·5162

The specific gravities (at 15·5° C.) of seven of these samples were determined, with the following results:—Maximum, 0·9436; minimum, 0·9411; average, 0·9420.

A detailed examination of eleven of these samples gave the following results:

	Browne test. Minutes.	Acid value.	Refractive index. (20° C.)
1.	11	3·23	1·5158
2.	11	3·46	1·5159
3.	12¾	7·21	1·5160
4.	12¼	6·70	1·5160
5.	12	8·23	1·5156
6.	10½	3·08	1·5172
7.	12½	8·56	1·5153
8.	11¾	6·46	1·5168
9.	10½	3·22	1·5178
10.	12¼	7·73	1·5160
11.	11½	7·57	1·5155

As was to be expected, the samples with the higher acid value showed a longer time of polymerisation. Standard samples of China wood oil, examined under the same conditions, gave a result of about 7 to 8 minutes. The refractive indices were in every case below the limit of 1·518, so that none of them, as judged by the ordinary standards, would be regarded as above suspicion, merely on the strength of these figures.

Correspondence with the Government Laboratory at Hong Kong revealed the fact that samples alleged to have been taken from the bulk deliveries of these oils had been submitted to the Government Laboratory and passed as being in accordance with the specification, but in no case had the sample been taken by the officials of the Laboratory.

Mr. Dovey was also good enough to re-determine the refractive indices of all the samples relevant to the shipments in question. In all, thirty samples were examined.

	Max.	Min.	Average.
Original Hong Kong oil, refractive index	1·5209	1·5182	1·5192
Re-determined, August 14th, 1930 ..	1·5210	1·5182	1·5191

The difference between the original and the re-determined refractive indices varied from —0·0007 to +0·0003. Only two samples showed the extreme variation of —0·0007, and, generally, the variation was of the order of ±0·0002. The results are of some interest as showing that the refractive indices of the oil do not alter to any appreciable extent on storage under normal conditions, even in the Tropics. It would also appear from these results that the native dealers use their refractometers to good effect and that, whatever may be the nature of a shipment, the sample which goes to the Government Laboratory is certain to pass the specification, and too much importance need not be attached to the Government report, unless the sample is actually taken by a properly accredited official.

As a general conclusion from the samples which I have examined, it would appear that Hong Kong wood oil frequently has a refractive index below the accepted minimum of 1·518, and that this may be due to the presence of oil from *A. montana*. It is not, of course, possible to come to a definite conclusion from a comparatively few samples which come from one source, but it would seem of some importance to investigate the matter further, with a view to definitely establishing this point. It is not suggested that the standard of the present specification should be reduced, but, if further investigation shows that the oil from *A. montana*, as obtained by the Chinese on a commercial scale, has normally analytical constants of the order of the values discussed in this paper, its presence in Hong Kong oils would account for the results here recorded, and the question how far the low refractive index and longer polymerising time are to be taken as indicating a lower quality, as distinct from adulteration, is, therefore, of some interest. Whilst the production of tung oil remains in the hands of the Chinese, it would seem impossible to separate the oils of the two species on a commercial scale, and, therefore, the oil of *A. montana* must be accepted as a normal constituent of the tung oil from the regions in which both species grow.

There is at present no recognised method of directly determining the presence of *montana* oil in China wood oil, and more work upon the characteristic properties of these two oils is a matter of considerable importance and interest. Whether the difference between the oils of the two species is sufficient to be of practical importance to the varnish maker—assuming, of course, equality as regards purity, etc., in other respects—is open to discussion.

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DISCUSSION

Mr. E. R. BOLTON said that the difficulty arose from the fact that most natural products exhibited natural variations, and, whilst the variations in a substance like milk were well known to every member of the Society, variations in tung oil were not so clearly appreciated. He hoped that the time was not far distant when tung oil would be bought and sold upon the proportion of elaeostearic acid, as being the constituent upon which its commercial value depended. The Imperial Institute had formed a Committee on tung oil (of which he was chairman); this, with financial aid from the Empire Marketing Board, had done much to encourage the production of tung oil in the Empire. He, therefore, sincerely trusted that no idea would arise that tung oil from British colonies was an inferior article, as it certainly was not. Mr. Bolton took the view that the discovery that certain oils obtained from *A. montana* were of lower quality than the average did not justify the author's suggestion that the standards should be widened and lowered. The Hong Kong Government Laboratory had recently taken steps which would most certainly have the effect of making adulteration more difficult, and it would be deplorable if we were to make it easier.

Mr. C. E. SAGE said that when adulteration of wood oil became prevalent, some 20 years ago, a method of sampling had been worked out, which, he thought, had considerably reduced the percentage of adulterated oil in commerce. In the case of commercial oils some definite relationship between analytical values and quality had been established, but for "home made" samples of oil one had to consider another set of standards altogether, for commercial oil must of necessity undergo some changes on keeping. Such oils might contain 5 to 6 per cent. of free fatty acid, but, personally, he avoided oils which contained over 3 per cent. Regarding the work done by the author of the paper, they were dealing with material obtained from young trees, and that would naturally differ from oils obtained from old-established trees which had been in the ground for years.

Dr. H. E. COX enquired whether there was any physiological explanation of the fact that oils obtained from immature trees, or, speaking generally, from trees grown in warmer countries, should have lower iodine values and refractive indices than those grown in colder climates. Apparently, the further south one went, the lower became these figures.

Mr. K. A. WILLIAMS thought that the variation of the constants of this Malayan oil from those of the Chinese oil was partly a climatic effect, as the characteristics of all oils were governed to a large extent by the temperature at which the plant grew. For example, linseed oil, having an iodine value of 180, could be produced in England, but soya bean oil, with an iodine value of 130, could not, because it required a slightly warmer country. If any particular oilseed were grown in different places, it was found that the colder climates produced oil of higher iodine value than the warmer ones; the exact constitution of the oil depended on the needs of the plant for the conditions under which it grew.

Mr. BARRY, replying, said that it would be seen from the figures quoted in the paper that excellent results had been obtained with oils from some parts of the British Empire, but, on the other hand, the unsatisfactory results obtained with oils from other parts were equally important from the scientific point of view.

The experiments showing the effects of local conditions upon China wood oil were particularly valuable, in view of the fact that the composition of that oil differed so remarkably from that of the seed oils with which it was often associated in industry.

In this connection the remarks of Dr. Cox and Mr. Williams were very suggestive. In the case of the ordinary seed oil the life cycle of the plant was completed within a single season, and the oil produced contained a series of aliphatic glycerides of varying degrees of unsaturation. It would appear that the plant, to some extent at least, adjusted itself to conditions by a variation in the proportion of the individual glycerides present in the oil. In the case of China wood oil, however, the life history of the tree producing it covered many years, and the oil consisted almost entirely of a single glyceride, namely, that of elaeostearic acid, which was characterised by its extreme sensitiveness to changes in physical condition and by an arrangement of its double-bonds which was unique among vegetable oils.

One would expect, therefore, that climatic and other conditions would have extremely interesting effects on the nature of the oil produced. As Mr. Sage had suggested, the age of the tree might also be expected to influence the nature of the oil to some extent, but it had to be admitted that the results obtained in America, where the subject has been most fully investigated, did not indicate that the difference was very material, providing, of course, the tree was properly cultivated and not exploited before reaching a reasonably mature age. It was not impossible that with increased knowledge of the properties and the best method of cultivation, commercially useful results might be obtained even in Malaya, although, for the time being, experiments had been discontinued.

The author was fully in agreement with Mr. Bolton that a distinction must be drawn between adulterated and abnormal oils. From the point of view of the consumer, the botanical origin of the oil was immaterial, for he was merely concerned with the properties which influenced the quality of his finished product, and the question, therefore, was not so much a matter of condemning oils as of grading them. If the acceptance or rejection of oil bought by a contract were based solely upon whether or not deliberate adulteration had been practised, the existence of dubious samples was a continual source of trouble and expensive litigation. On the other hand, if supplies were purchased on a definite specification, this question of adulteration was, to a large extent, avoided. At the same time, the analyst could not ignore the existence of abnormal samples, whether dealing with China wood oil or with other natural products. The recognition of the distinction between abnormal and adulterated samples not only determined the attitude of the State towards the producer of the article in question, but also made it possible to trace the cause of abnormality to its source, and in most cases eventually to reduce, if not entirely to eliminate it.

Experiments on the Quantitative Separation of Pilocarpine from Quinine by Means of Gallotannin

BY M. NIERENSTEIN, D.Sc.

(*Work done under the Analytical Investigation Scheme*)

IN a previous communication from this laboratory (Fear, ANALYST, 1929, **54**, 317) it was shown that, of twenty-six alkaloids examined, only quinine, cinchonine, cinchonidine, strychnine, brucine and caffeine were precipitated by gallotannin. This suggested the possibility that gallotannin might prove a quantitative reagent for the separation of these two types of alkaloids, and pilocarpine and quinine were chosen as representative examples. Unfortunately, it was found at an early stage of the investigation that as much as 15 to 18 per cent. of pilocarpine could not be accounted for when precipitating, with gallotannin, the quinine from a solution containing pilocarpine (base) and quinine hydrochloride. This discrepancy, as subsequent work has proved, is due to the fact that quinine gallotannate (and this will probably also apply to the other gallotannates) adsorbs pilocarpine.

1. PREPARATION OF QUININE GALLOTANNATE.—The gallotannin used was purified according to Fischer (*Ber.*, 1912, **54**, 915) and tested for *free* gallic acid by Mitchell's method (ANALYST, 1923, **48**, 2), as modified by Nicholson and Rhind (*ibid.*, 1924, **49**, 507). It contained 3·8 per cent. of gallic acid, but it was found that by prolonged washing with ether the free gallic acid content could be reduced to 0·7 per cent., after which further washing with ether seemed to have no further effect. The quinine gallotannate was prepared by adding a 2 per cent. solution of gallotannin solution to a 1 per cent. solution of quinine hydrochloride in water, collecting the precipitate with the aid of a suction pump, washing with ether, and drying at 100° C. Quinine gallotannate is hygroscopic, and is best kept in a vacuum desiccator over phosphorus pentoxide.

2. DETERMINATION OF PILOCARPINE.—Solutions of 2 grms. of pilocarpine (base) in 100 c.c. of distilled water were used in all the experiments. Such a solution has $[\alpha]_D^{18} = +106°$ according to Schmidt (*Die Alkaloide*, 1920, p. 580), but, as the result of a series of observations made in this laboratory, the constant $[\alpha]_D^{18} = +109·5°$ was adopted. The aqueous solution (50 c.c.) was extracted four times with 50 c.c. of ether free from alcohol (B.D.H. Purified Ether, sp. gr. 0·720), and the collected extracts were dried over sodium hydroxide for ten days and evaporated. The residue was then left standing in a vacuum desiccator for eight days over paraffin, until constant in weight. The error, based on 28 determinations, was found to be ±1·3 per cent.

3. ACTION OF QUININE GALLOTANNATE ON PILOCARPINE.—Solutions of pilocarpine (50 to 125 c.c.) were shaken for 2 to 16 hours with quinine gallotannate

(2 to 12 grms.), filtered and extracted with ether, proportional quantities of ether being used. In this manner it was found (32 determinations being made) that 8·3 to 19·2 per cent. of pilocarpine had been adsorbed by the gallotannate, the adsorption apparently depending on the length of time of shaking.

It might be pointed out that the quinine gallotannate does not undergo disintegration during the process of adsorption, since the rotation of the pilocarpine, if interpolated, remains $[\alpha]_D^{18} = +109{\cdot}5^\circ$ when adsorbed by quinine gallotannate. This was found to be the case in all the experiments mentioned above. Since quinine is laevorotatory, there would have been a fall in the rotation if quinine had been set free. The values obtained for pilocarpine, after adsorption by quinine gallotannate, are thus not affected by the presence of quinine.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

DETECTION *IN SITU* OF TIN SOLDER CAUSING DARK DISCOLORATION IN CHEESE

SAMPLES of cheese showing areas of dark pigmentation around specks of foreign material are occasionally encountered. The cause may be due to small particles of lead-containing material slowly dissolving and diffusing through the cheese, lead sulphide being deposited by the interaction of small amounts of hydrogen sulphide formed during cheese ripening (Leitch, *Scot. J. Agr.*, 1927, **10**, 165). Cheese may be contaminated with traces of lead or lead compounds either as a rare impurity in annatto (in coloured cheese), as red lead from pipe joints, or as abraded solder from unions, seams or other source. The detection of lead in the amount necessary to cause the trouble in cheese is difficult, often indefinite, and sometimes impossible (see the "triple nitrite test" described by Fairhall, *J. Biol. Chem.*, 1923, **57**, 455). But when such cases are due to particles of solder, advantage can be taken of the sensitive "molybdenum blue" test for the tin accompanying the lead in the solder (Munro, *Proc. Nov. Scot. Inst. Sci.*, 1927, **16**, **9**). The test can be carried out *in situ* on the dark areas in a thin section of cheese.

A section of cheese showing darkened area and, if possible, the exposed nucleus, is moistened with water on a watch glass, and a drop of 0·5 per cent. solution of ammonium molybdate in *N* hydrochloric acid is added, followed by a drop of 5 per cent. sodium phosphate solution (bench reagent). If tin is present, an intense blue colour will develop in a short time around the nucleus, growing fainter towards the edges of the patches. The blue colour will be seen to concentrate in the veins between the particles of curd, which stand out clearly against the darker blue boundaries. A positive test for tin in the dark patch is an indication that solder is present, the lead of which is responsible for the discoloration. Cheese not contaminated with tin in this manner does not develop any blue colour, only a faint green tinge forming within an hour of carrying out the test.

The metals likely to get into cheese during manufacture are tin, lead, iron and copper. If a particle of copper (metal) is embedded in cheese, its presence in the ripened cheese will be shown by the formation of a strong *green* halo round the particle. This would be true for any copper alloy, also. This has been met with in practice.

Particles of iron or of iron rust do not form black discolorations; and, although the particles are often discernible to the naked eye, they are looked on as "dirt," or "foreign matter," and classed with particles of straw, rubber, etc., as accidental impurities.

Lead is the metal causing discoloured areas which usually are responsible for lowering the marketable value of the cheese, and the object of the present note is to detect the entry of solder into cheese by testing for tin. The tin in cheese is undoubtedly in the stannous condition, since (*a*) the oxygen tension in cheese is of a very low order, and oxidation of stannous salt would be improbable, and (*b*) tin slowly dissolving from metallic tin would be in the stannous condition. Even exposure of a section of cheese to the air for a considerable length of time before testing would not change the tin salt into the stannic condition, especially in the presence of elementary tin in the nucleus.

W. L. Davies.

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Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

SUITABILITY OF WATER SOFTENER FOR HAIR-DRESSING PURPOSES

On October 20th, 1931, a claim was brought by a firm of engineers in the High Court before Sir W. Hansell, K.C., Official Referee, for the balance of the price of an automatic water-softening machine which had been supplied to a firm of hairdressers. The defendants admitted the claim, but pleaded that the machine produced water which was wholly unsuitable for their purposes, as it could not be used for waving hair, but left it sticky.

Dr. H. S. Hatfield pointed out what he regarded as defects in the plaintiffs' machine.

An assistant in the hairdresser's firm gave evidence that after water from this machine had been used the hair was sticky and could not be combed, and there were complaints of the "permanent wave" coming out in a week. When natural soft water was used there were no complaints, and complaints stopped after the use of this machine was discontinued.

Mr. C. E. Sage, F.I.C., said that he had analysed the water in question. He would not describe it as soft water, but as "treated" water, which he would not care to drink. His objection to it was the absence of lime and the presence of soda.

Mr. W. H. Simmons, B.Sc., F.I.C., said that he had experimented with human hair immersed in water containing 17 parts per 100,000 of sodium carbonate, and was of opinion that such a water as was produced by this softener would not adversely affect the process used by the defendants. Such water was also, he considered, perfectly suitable for human consumption.

On October 26th, Sir W. Hansell, giving judgment, said that the description given by the selling agent of the plaintiffs, who said that the machine was automatic and suitable for hairdressers, did not amount to a warranty, but was only of the nature of description, persuasion and puff. The machine was automatic, and any trouble in its working appeared to be due to the fact that when it was installed the defendants had not appreciated the fact that the water pressure was not suitable. The defendants had failed to satisfy him that anyone had suffered any ill effects through drinking the water, and, in any case, there was no warranty that the water was potable.

There was considerable conflict of evidence as to whether the water was fit for the purpose of hairdressing, and the defendants had failed to satisfy him that it was not suitable. If he had to decide why there were occasional failures in the hair-waving operations, he would say that they were due either to the health of the lady on whom the wave refused to stay, or to the fact that the soap had not been sufficiently rinsed away. If he were wrong, the sum of £20 would amply compensate defendants for any damage sustained. There would, therefore, be judgment for the plaintiffs.

A stay of execution was granted with a view to an appeal.

New South Wales

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1930

THE Acting Government Analyst (Mr. S. G. Walton) reports that 22,194 samples were examined during the year ending December 31, 1930, of which 19,705 were samples taken in connection with the Pure Food Act, 1908. By far the greater proportion of the food samples were milks, of which 14,638 (351 adulterated) were collected in the Metropolitan area, and 2747 (159 adulterated) in country districts. Among the subjects dealt with in the Report are the following:

BUTTER SUBSTITUTES AND THE MARGARINE STANDARD.—Samples of "butter" submitted were found to contain large proportions of coconut fat. This was apparently part of a systematic attempt to evade the provisions of the regulations governing butter and margarine (butter substitutes). The standard for margarine requires that all preparations of edible oil or fat which are intended to be, or which may be, used in place of butter, shall be marked "Margarine," and, also, to permit of easy identification, the standard requires that such preparations shall contain specified proportions of sesame oil or Queensland arrowroot. The butter-fat content, moreover, is limited to 10 per cent. When an article is prepared for use as butter, which is not marked "Margarine," and which does not contain the ingredients specified in the standard for margarine, it must be in conformity with the requirements of Regulation 27, *i.e.* it must be butter. The samples under notice were not marked "Margarine," did not contain either Queensland arrowroot or sesame oil, and approximately 25 per cent. of butter was present as one of the constituents. The following is a representative analysis:—Water, 15·8; curd and salt, 2·3; fat, 81·9 per cent. The values from the fat were: Reichert-Wollny value, 13·9; Polenske value, 13·0; Kirschner value, 6·5; iodine value, 9·5; and saponification value, 251. From these results it was concluded that the fat was prepared chiefly with coconut fat, and contained approximately 25 per cent. of butter.

STANDARD FOR CITRUS FRUIT JUICES.—The extraction of citrus fruit juices for the cordial trade is almost wholly done by mechanical means. There is, therefore, a tendency to include with the juice, rind, pith and segment partition walls in a finely divided state. For the purpose of prescribing the maximum amount of insoluble solids which should be allowed in citrus fruit products (beverages), analyses were undertaken, the results of which are given hereunder. The method used was that given in the "A.O.A.C. Methods of Analysis" (1925 edition, p. 210), for water-insoluble solids in fruit products, excepting that, before weighing, the insoluble matter was separated from the hardened filter paper used, by washing it with a jet of hot water into a dish in which it was evaporated to dryness and weighed. The following results were obtained:

	Insoluble solids. Per Cent.
Orange juice (a good mechanically extracted juice)	1·0
Lemon juice („ „ „ „)	0·6
Lemon juice expressed in laboratory (1 doz. lemons of average quality were deprived of their skins, and, as far as possible, freed from adhering pith. They were then pulped, this pulp containing all the coarse segment partition walls and juice cells)	2·2
Lemon juice expressed in laboratory (1 doz. lemons of similar quality to those above were squeezed in an ordinary glass squeezer. This juice represents an ordinary lemon squash containing practically all the juice cells, but not the segment partition walls)	0·5

After consideration of these figures it was decided that, in order to prevent the addition of rind, pith and segment partition walls to citrus fruit juices, the following standards should be recommended:

Orange juice: Insoluble solids to be not more than 1·5 per cent.
Lemon juice: „ „ „ „ „ „ „ 1·0 „

STANDARD FOR JAM.—With a view to formulating a suitable standard for jam, samples differing in quality were examined, the following results being obtained:

	Strawberry conserve. Per Cent.	Strawberry conserve. Per Cent.	Raspberry jam. Per Cent.	Raspberry jam. Per Cent.
Moisture (loss at 100° C.)	21·5	42·9	20·65	25·56
Total solids	78·5	57·1	79·35	74·44
Insoluble solids	1·0	1·6	3·13	3·18
Alcohol precipitate (pectin, etc.) ..	0·27	0·39	0·24	0·31
Total acidity (as citric acid)	0·59	0·60	0·90	0·82
Malic acid .. Not more than	0·1	0·1	0·1	0·1
Citrates (as citric acid)	0·72	1·07	1·09	1·27

The question of permitting the addition of various fruit derivatives to jam, with a view to improving manufacture without lowering the quality, was considered. Where the fruit used, through seasonal or other cause, is deficient in those natural qualities (acid, pectin, etc.), on which the flavour and appearance of the finished product depend, it appears reasonable to allow the addition of limited amounts of these substances in order to ensure the manufacture of a better and more uniform article. Moreover, recent investigation has shown that acid is necessary for the conversion of pectose into pectin. As, however, the indiscriminate use of acid and pectin might result in lessening the quantity of fruit used, it is necessary, if the use of these substances is to be sanctioned, to prescribe a minimum fruit content. After consideration of all the facts, it was recommended that the standard should provide for a fruit content of not less than 45 per cent. (by weight), and should permit the addition of up to 0·3 per cent. of pectin (calculated as calcium pectate) and of 0·5 per cent. of fruit acids.

USE OF SAPONIN IN BEVERAGES.—During the year a sample of "heading," used for promoting froth on beverages, was received for analysis. This was found to be a solution of saponin, probably obtained from quillaia bark. The saponins derived from this source are stated to contain toxic glucosides (quillaic acid and sapotoxin), and the presence of any glucoside must, in accordance with the requirements of Regulation 66 (1), be declared on the label.

Substances similar to this have been universally used for the production of froth on temperance and other drinks for a very long period. Although saponin has well-defined toxic properties, it is recognised that the mucous membrane of the digestive canal forms an almost complete protection to limited amounts of it, and, therefore, it is unlikely that harmful results would ensue from the quantities at present being used in beverages. If, however, its continued use is to be allowed, it is desirable that the maximum amount permissible should be specified.

Experiments as to the toxicity of the sample submitted were carried out as follows:—A guinea pig weighing 472·5 grms. was "drenched" with 1 c.c. of the sample, and was not affected after twenty-four hours. The same animal was then "drenched" with 5 c.c. It showed extreme distress after one and three-quarter hours, and died within two hours. On examination the stomach showed a large patch of haemorrhage in the wall; congestion in the upper third of the intestines; slight congestion of the spleen and liver. The kidneys and suprarenals were normal. The stomach and part of the intestines were very considerably distended with froth, and the heart was very full. Apparently the immediate cause of death was the pressure on the heart from the enormously distended stomach.

SACCHARIN IN FOOD.—The substitution of saccharin for sugar has lately become increasingly noticeable. An examination of pickles, made in 1929, disclosed the fact that practically all the locally-made articles contained this substance, manufacturers urging in its favour that the public demanded white, sweet pickles, which could only be supplied by the substitution of saccharin for sugar in manufacture. It was stated that when sugar is used, reaction with acetic acid causes discoloration and renders the article unattractive.

In 1930 it was found that saccharin was used by manufacturers in this State in the preparation of ice-cream cones. The reason given for the substitution in this instance was that cones containing the requisite amount of sugar became soft on exposure, and in that condition proved unsatisfactory containers for ice cream.

A representative number of cordials was examined for the presence of saccharin, but in only two cases, both of which were of country manufacture, was saccharin found.

PERSULPHATES IN BREAD IMPROVERS.—Four samples of yeast foods submitted were found to contain persulphate in amounts ranging up to 3 per cent. The use of this "improver" in flour is a recent innovation in this State, and was the cause of a severe outbreak of bakers' dermatitis in employees handling these substances. Action has been taken, as a consequence of which the use of persulphates as a constituent of yeast foods has been abandoned.

Cyprus

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1930

THE Government Analyst for Cyprus (Dr. S. G. Willimott) reports that the year 1930 was the busiest since the Government Laboratory was opened in 1901, because of the re-organisation of the laboratory and the construction of separate laboratories for analytical work, forensic investigations and water analysis. The official work consisted of the usual analyses and examinations in connection with criminal cases, counterfeit coins, samples under the Food and Drugs Law of 1926, samples for water analysis, customs and excise, animal viscera for poison and a miscellaneous collection of samples for private analysis. The total number of analyses made was 1546, as compared with 1713 in 1929, the reduction being due to pathological specimens now being dealt with in the Bacteriological department, so that the year's analytical work shows an increase of 50 per cent. Some 631 exhibits were examined in connection with 168 criminal cases.

HASHISH TRAFFICKING.—It is some years since so many important cases of trafficking in hashish, contrary to the Dangerous Drugs Law, were investigated. Three such cases came before the District Court of Limassol. In each case the material in question was identified as hashish of second quality, probably originating in Syria. The defence that this material was some substance other than hashish failed in each case and convictions were recorded.

FORENSIC WORK FOR THE POLICE.—Under the present system many frivolous, even ridiculous, cases are sent in indiscriminately by the Police for investigation, and it is calculated that only about 6 per cent. of this work is of any real value to the Crown. In Palestine, where a very similar problem arose, the difficulty was solved by placing with the Attorney-General's Department the authority for having exhibits examined in the Laboratory.

MUSHROOM POISONING.—An investigation of poisonous fungi arose in connection with two important outbreaks of mushroom poisoning at Lefkoniko and Larnaca; in the former case ten people died, and in the latter one person. From the forensic point of view, the Larnaca case was of special interest because an alkaloid of the nature of muscarine, the poisonous principle of certain fungi, was isolated from the viscera. By investigating the species and habitat of both edible and inedible species of Cyprus mushrooms, it was possible to carry the investigation a stage further. Poisonous types were also examined for their content of alkaloids of the muscarine group.

COUNTERFEIT COINS.—The 54 counterfeit coins examined appear to fall into two distinct categories, *viz.* one consisting of coins composed of practically pure tin, and the other of coins of silver and copper, the silver varying between 60 and 80 per cent. This comparatively high percentage is probably explained by the low price of silver at present prevailing.

BARIUM CARBONATE IN ANIMAL POISONING.—Eighteen viscera, taken from ox, sheep, mule or donkey, were analysed, but one only (sheep) was found to contain a poisonous substance. This was identified as barium carbonate. This chemical finds considerable use in Cyprus as a rat poison, and accidental poisoning of animals by this means is very liable to occur.

FOOD SURVEY OF CYPRUS.—A food survey of Cyprus was carried out during the last six months of the year. The objects of the survey were to ascertain, as accurately as possible, the real adulteration rate prevailing in the Colony and to obtain sufficient analytical data on local products to frame scientific standards for the staple foodstuffs. Accordingly, a large number of samples was collected both in town and village throughout the six administrative districts. It was arranged, through the police, to take samples every week in the Nicosia district, and every fortnight in the five remaining districts. Altogether, 610 official samples were analysed during this experiment, that is, the largest figure recorded for any half-year. The minimum rate of adulteration found was 8·3 per cent., which figure will probably be increased when the milk data, which it is hoped to obtain in 1931, can be included in these results. As in previous years, the principal commodity adulterated was coffee, 49 of 163 samples being condemned.

WATER SUPPLY OF CYPRUS.—There can be no question that this is one of the most urgent sanitary problems in Cyprus to-day. Of 70 samples arising from all six districts, six were found on analysis to be unfit for drinking purposes. The samples examined this year included many from new sources of supply located principally in the villages. Increasing knowledge of local water supplies indicates the impossibility of applying any rigid European standards to Cyprus waters. Indeed, to do so would be equivalent to condemning most of the water sources in the Island. It is true that both chemical and bacteriological data point to the existence of very pure water supplies in the mountain areas, but only too frequently such waters become more or less contaminated by the time they reach the consumer, the root of the trouble being the incidental contamination of unprotected water-courses, faulty aqueducts or open wells. There is undoubtedly great need in Cyprus for a scientific water survey, especially as no official standard of any description exists for potable water-supplies.

"CRUDE PETROLEUM."—Thirty-nine samples were submitted by the Customs and Excise Department as "crude petroleum," according to the Law. Some difficulty arose in connection with the samples coming within this category. The importation of solar oil as fuel for gas engines increased very considerably during the year, and since it was found, as the result of laboratory tests, that it frequently gave a reasonable illumination when burnt in an ordinary lamp, the oil in question became legally dutiable. This imposed some hardship on the farmer, who was the principal consumer, and created an obstacle to agricultural development. The real difficulty, however, lies in the unsatisfactory condition of the law as it relates to petroleum products. A confusion of terms appears to have sprung up, namely, to confuse crude petroleum, as it exudes from the well, with the various less refined petroleum products, ranging from solar oil to Diesel oil. The difficulty may be removed either by evaluating such petroleum products on the basis of analysis and by the recognition of definite scientific standards, or by remitting altogether the duty on petroleum products other than kerosene and benzine.

Commonwealth of Australia

COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

DIVISION OF FOREST PRODUCTS*

No. 1. IDENTIFICATION OF WOOD BY CHEMICAL MEANS. PART I

The limitations of methods of identification of woods are emphasised, with special reference to the hardwood genus *Eucalyptus*, of which over 300 species are known in Australia. Chemical tests, which may supplement microscopical methods, are reviewed. Thus, Kanehira (*Bureau of Productive Industries, Formosa*), estimates flavone content from the colour produced on reduction of 10 c.c. of an alcoholic extract of the wood in the presence of hydrochloric acid, magnesium powder and a drop of mercury, and so places the wood in one of 3 categories according to the intensity of the colour. Welch (*J. and Proc. Royal Soc., N.S.W.*, 1922, **56**, 241) has also attempted to distinguish groups of this genus by tests on aqueous and alcoholic extracts with reagents such as ferric chloride, sodium hydroxide, lime water, etc., but the method requires further systematisation and standardisation on a large number of samples of known origin, especially in cases where the species are botanically similar (*vide infra*).

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* Technical Papers, Nos. 1, 2 and 3, 1931. Nos. 1 and 2, by H. E. Dadswell; No. 3, by W. E. Cohen and H. E. Dadswell.

Improved tests on the lines of Welch's experiments showed that considerable variations may occur even with different samples from the same species, but that previous knowledge of the chemical composition may assist in the development of a simple test.

IDENTIFICATION OF KARRI (*E. diversicolor*) AND JARRAH (*E. marginata*).—(1) The standard procedure of the U.S. Forest Products Laboratory was employed (Schorger, *Chemistry of Cellulose and Wood*, 1926), and 34 samples of jarrah and 17 of karri were shown to have cellulose contents (on an oven-dry basis) of 35·4 to 51·6 (mean 44·5) and 53·0 to 62·7 (mean 59·0) per cent., respectively. (2) A simpler test is to burn a splinter of the untreated sound heart-wood the size of half a match. Karri (150 samples) burned well, with glowing, to a white ash, whilst jarrah (200 samples) always burned poorly without glow, and left little or no black ash. (3) The ash content of 5 grms. of sawdust was determined by ignition in a platinum dish, the residue was dissolved in excess of warm 0·1 *N* hydrochloric acid, and the mixture was back-titrated with 0·1 *N* sodium hydroxide solution to phenolphthalein. Karri (29 samples) gave 0·12 to 0·86 (mean 0·30) per cent. of ash, having an alkalinity of 0·33 to 1·57 (mean 0·63) c.c. of 0·1 *N* acid per grm. of oven-dry wood, and jarrah (58 samples) 0·04 to 0·49 (mean 0·14), and 0·00 to 0·16 (mean 0·06), respectively. These methods, especially (2) and (3), are effective only if unweathered and untreated wood is used; weathering changes the ash content to a greater extent than the cellulose figure.

IDENTIFICATION OF TALLOWWOOD (*E. microcorys*), BLACKBUTT (*E. pilularis*) AND WHITE MAHOGANY (*E. acmenioides*, *carnea* and *umbra*).—(1) The mean ash contents were 0·27, 0·16 and 0·09 per cent., and their alkalinities 0·42, 0·05 and 0·02 c.c., respectively. In one (abnormal) case only was the alkalinity of a tallowwood ash lower than those of the other two species. (2) About 2 grms. of sawdust are heated with 20 c.c. of alcohol for 2 minutes, and the extract is cooled, filtered and diluted with 20 c.c. of water. Tallowwood gave a definite white turbidity, blackbutt a clear solution, and white mahogany an immediate turbidity which, unlike that from tallowwood, was subsequently filterable.

IRONBARK GROUP (15 samples).—Ash-alkalinity values were:—*E. sideroxylon*, *propinqua* and *punctata*, below 0·16 c.c.; *E. paniculata*, above 0·78 c.c. (49·0 to 56·0 per cent. of cellulose); *E. siderophloia*, 0·35 to 0·05 c.c.; *E. crebra*, 0·90 to 0·32 c.c. (35·4 to 46·3 per cent. of cellulose). The dilution test is positive for *E. sideroxylon* only.

RED BOX (*E. polyanthemos*) AND RED GUM (*E. rostrata*).—If 0·5 c.c. of a 1 per cent. solution of sodium hydroxide is added to 5 c.c. of an alcoholic extract of the sawdust after pre-extraction in hot water, yellow and chocolate-coloured precipitates are produced, respectively (7 samples).

NO. 2. DENSITY OF AUSTRALIAN TIMBERS

The sp. gr. of the solid woody material constituting timber is 1·52, though that of the actual timber depends on the number, size, form and arrangement of the wood cells. These cells contain water and shrink on drying, and methods for the determination of density must take such shrinkage and water into account. Methods are usually based on the weight of the oven-dried sample in relation to the volume after oven-drying, or on similar ratios for air-dried or green (*i.e.* the living) wood, the last being of value only when green timber is available (see "Methods of Testing Small Clear Specimens of Timber," *Brit. Eng. Stds. Assoc.*, Specification No. 373, 1929). Modification of these methods are also used.

None, however, is suitable for the identification of Australian timbers, since these differ in moisture-content, and, in some cases, it is unlikely that two pieces of wood from the same stick will collapse on drying in the same way. The oven-dry weight and volume after soaking were therefore determined instead.

Method.—Three adjacent cross-sections (0·25 to 0·5 inch thick), cut at least 2 inches from one end of the block, were kept together and trimmed to 2·5×1 inch, so as to obtain only sound heartwood. All were then immediately scraped free from dust and splinters and placed in an air-tight container, the two outer blocks (*M*) being weighed together and heated at 105° C. until constant in weight, whilst the centre portion (*D*) was immersed in water until it had attained a constant volume (*e.g.* 6 days if 11 per cent. of water was originally present). *D* was then wiped dry on the outside, and the new volume was determined in the usual way from the displacement, as given by the buoyant force exerted by the sample when immersed in water. Then oven-dry weight of *D*=(original weight of *D*×oven-dry weight of *M*)/(original weight of *M*); and sp. gr. = 62·5× (calc. oven-dry weight of *D*)/(volume after soaking) in lbs. per cubic foot. It was shown that even with highly dried *E. regnans*, a timber in which collapse on drying is very prevalent, soaking causes the volume to return to its "green" dimensions. Green samples should be given the same treatment, since slight collapse may occur even with high moisture-contents. Determination of oven-dry weight after soaking is not recommended, owing to the possible loss of extractives, nor is it advisable to use the same piece of timber for both oven-drying and soaking, unless the sample is very small, in which case the former value should be determined first.

Data.—*E. crebra*, 56·1 (mean sp. gr. in lbs. per cb. ft.); ***sideroxylon*** (red iron-bark), 54·9; ***siderophloia***, 57·4; ***paniculata***, 55·7; ***polyanthemos***, 54·9; ***rostrata***, 43·6; ***resinifera***, 45·9; ***gomphocephala***, 51·4; ***patens***, 42·7; ***redunca*** (var. ***elata***), 57·9; ***accedens***, 57·4; ***salubris***, 55·1; ***salmonophloia***, 56·0; ***tereticornis***, 48·5; ***marginata*** (jarrah), 41·6; ***sieberiana***, 45·8; ***obliqua***, 35·4; ***gigantea***, 34·1; ***regnans*** (mountain ash), 27·9; ***pilularis***, 44·3; ***microcorys***, 51·8; ***diversicolor***, 37·9 to 46·1. The values for karri and jarrah are lower than those obtained by the oven-dry weight/volume method. The sp. gr. decreases slightly with increase in height of the sample from the ground (about 3 units between 5 and 35 feet).

No. 3. Study of Lignin Determination

According to the U.S. Forest Products Laboratory (Mahood and Cable, *J. Ind. Eng. Chem.*, 1922, **14**, 251), 2 grms. of air-dried sawdust (80 to 100-mesh) are extracted for 4 hours with a mixture of benzene and alcohol (2 : 1) to remove resins, gums, kinos, etc., and the residue is dried and digested for 16 hours with cold 72 per cent. sulphuric acid. The acid is then diluted to 3 per cent., the mixture boiled under a reflux condenser for 2 hours, and the final residue (lignin) filtered on a tared alundum crucible, washed free from acid with hot water, dried at 105° C. and weighed. The method appears to be successful with North American hardwoods, but Australian woods gave high lignin contents with wide variations for one species. This was shown by microscopical methods to be due to dark-coloured substances in the vessels, ray cells, wood parenchyma and lumina of the wood-fibres, which are only partly soluble in the mixture of benzene and alcohol, and in the acid, and are therefore weighed with the lignin. Qualitative tests with various organic and inorganic solvents led to the following procedure:—

Sampling.—The standard (U.S.) method is unsatisfactory, since the above resinous materials are brittle and grind to a fine powder which tends to pass to a disproportionate extent through the finer sieve. An entire block was therefore sawn into strips and ground in an impact mill until the whole sample (about 200 grms.) passed a 100-mesh sieve. The mill failed to grind a small amount which was rejected.

Method.—About 3 grms. of sample in a 300-c.c. conical flask with an air-condenser were heated with 100 c.c. (150 c.c. for jarrah) of 0·125 *N* sodium hydroxide solution for 80 minutes on the water-bath, and the residue was filtered off at once in a tared alundum crucible and washed free from alkali with hot water. The washing could be expedited by one preliminary wash with 10 per cent. acetic acid. In the experimental work the residue was dried at 105° C. and weighed in order to determine the alkali-soluble material, but, normally, the lignin determination by the standard acid digestion method is carried out on the washed residue.

Weaker alkali is not recommended, since it requires a longer digestion period, whilst stronger solutions may attack the wood structure. Successful results were obtained with Canadian hemlock (26·4 per cent. on the oven-dry weight of the original sample), Canadian spruce (24·8), jarrah (21·7), red ironbark (20·5), and mountain ash (21·4). Lignin in hemlock and spruce is more resistant to the alkali than that in the other woods, although with these the attack is so slight that the accuracy of the method is hardly affected. The above results were confirmed by microscopical methods.

J. G.

United States Department of Agriculture

SERVICE AND REGULATORY ANNOUNCEMENTS

STANDARD FOR CANNED TOMATOES*

CANNED tomatoes are the normally flavoured and normally coloured canned food consisting of the peeled, cored, and trimmed, whole or large pieces of the mature red fruit of the tomato vine (*Lycopersicum esculentum*), with or without the drained juice of peeled, cored, and trimmed tomatoes in amount not exceeding that normal to the fruit being packed, and with or without added seasoning (sugar, salt).

Meaning of Terms.—The fruit shall be considered as whole or in large pieces when at least 45 per cent. of the total contents will be retained after draining for two minutes on a sieve[1] having 2 meshes to the inch. On containers of less than 3 pounds net weight, sieves 8 inches in diameter are used. On containers of 3 pounds net weight or more, sieves 12 inches in diameter are used.

The fruit shall be considered normally coloured when a sample at least 1 inch deep of the homogeneous pulped meats shows a red colour containing at least 58·0 per cent. red and not more than 37·3 per cent. green, in terms of the three primary colour distribution curves of the Optical Society of America, referred to Abbott-Priest standard white light.[2] In performing this test the material retained on the 2-mesh sieve is pulped and freed from air bubbles. It is then placed in a black container, and visible seeds are removed by skimming or pressing below the surface.

The fruit shall be considered as peeled when there are not more than 1·5 square inches of peel per pound of net contents.

The fruit shall be considered as trimmed when the total exposed area of unsightly blemishes, such as scars or brown or black coloured portions, does not exceed one-fourth square inch per pound of net contents.

Substandard Designation.—Canned tomatoes which fail to meet the above standard shall, except as hereinafter provided, bear the legend for low quality promulgated by the Secretary of Agriculture.

Exceptions.—Canned tomatoes which fail to meet the above standard only in that they contain added pulped and strained tomato material need not bear the low-quality legend if labelled "tomatoes with purée from trimmings."

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* Food and Drug No. 1, Rev. 4, issued May, 1931, p. 6.

[1] Wire of a uniform diameter, not less than 0·04 nor more than 0·07 inch.

[2] These percentages do not refer to the proportion of "red" to "green" tomatoes in the container. They are rather the precise physical terms necessary to define colour accurately in a legal standard. Conformity to the minimum colour requirement may be conveniently judged by certain commercial colour measuring devices For example, the colour of a given sample may be matched by the following combination of Munsell colour discs:

(1) 5R 2.6/13 (glossy finish).
(2) 2.5YR 5/12 (glossy finish).
(3) N 1/ (glossy finish).
(4) N 4/ (glossy finish).

If the exposed area of disc (1) covers one-third or more of the circle, and the exposed area of disc (2) does not exceed that of (1), the sample meets the minimum colour requirement, regardless of the exposed area of discs (3) and (4).

STANDARD FOR SALT.*

1. Table salt (dairy salt) is fine-grained crystalline salt containing, on a water-free basis, not more than 1·4 per cent. of calcium sulphate ($CaSO_4$), not more than 0·5 per cent. of calcium and magnesium chlorides ($CaCl_2$ and $MgCl_2$), nor more than 0·1 per cent. of matters insoluble in water.

Pending further announcement, no exception will be taken by the Food and Drug Administration to table salt that meets the requirements of the standard except that it contains anhydrous calcium sulphate (anhydrite) in excess of 0·1 per cent., provided that the total calcium sulphate content does not exceed 1·4 per cent.

STANDARD FOR BAKING POWDER.*

Baking powder is the leavening agent produced by the mixing of an acid-reacting material and sodium bicarbonate, with or without starch or flour.

It yields not less than 12 per cent. of available carbon dioxide.

The acid-reacting materials in baking powder are: (1) Tartaric acid or its acid salts, (2) acid salts of phosphoric acid, (3) compounds of aluminium, or (4) any combination in substantial proportions of the foregoing.

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* Food and Drug No. 2 (Second Revision), issued September, 1931, p. 19.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Eggs Rich in Iodine. A. Jaschik and J. Kieselbach. (*Z. Unters. Lebensm.*, 1931, **62**, 572–575.)—The whites and yolks of 14 eggs are mixed well with lime water in a large iron dish and dried at 100° C., and the residue is ground with lime water, sodium carbonate and excess of a mixture of magnesium oxide and acetate, and again dried and gently ignited. The mixture is then extracted with hot water, and any residue is again gently ignited and extracted, the combined aqueous extracts being finally evaporated and ignited once more at a low temperature. This new residue is extracted with hot alcohol and then dissolved in 2 c.c. of water, and this solution is acidified with phosphoric acid, and a drop of fresh 0·1 per cent. solution of sodium nitrite is added. If the mixture is then shaken in a stoppered tube (8 cm. long and 12 mm. in diameter, with a capillary 3 cm. long and 8 mm. in diameter at one end) with about 0·5 c.c. of carbon tetrachloride for every 0·25 to 1·00 mgrm. of iodine present, the solution of iodine in the solvent may be transferred to the capillary portion by centrifuging, and the colour matched against that produced by a similar procedure from a standard solution (Zahoránszky, after von Fellenberg, *Volksernährung*, 1930, **5**, 323; *cf.* Andrew, ANALYST, 1930, **55**, 269). Larger quantities may be titrated. The ordinary eggs of Leghorn hens (mean weight of shell 8·3, white 31·6, and yolk 18·9 grms.) yielded 24·2γ of iodine per kilo. or 1·4γ per egg, of which only a trace came from the white. Addition of the equivalent of 1·5 mgrm. of iodine per day to the diet of each hen for 2 months produced an egg with a thinner shell (mean weight 7·1 grms.), containing 31·1 grms. of white and 18·3 grms. of yolk.

The iodine content was 2·981 mgrms. per kilo., or 168·5γ per egg (15·6γ in the white, and 152·8γ in the yolk). Other authors (*loc. cit.*) have found 10 to 63γ per kilo. (0·5 to 2·5γ per egg) for ordinary eggs. J. G.

Determination of the Colouring Matter of Egg-Yolk. A. Terényi. (*Z. Unters. Lebensm.*, 1931, **62**, 566–571.)—Lutein, $C_{40}H_{56}O_2$, the yellow colouring matter of egg-yolk and an isomer of xanthophyll, is best determined by thorough extraction of 1 to 2 grms. of the ground yolk (separated from the white and shell) with three 30-c.c. portions of a mixture of equal volumes of alcohol, ether and petroleum spirit. Any lumps are broken up with a glass rod, and, after 15 to 30 minutes, each successive mixture is filtered into a 50-c.c. flask until this is filled to the mark. The colour of this extract is matched in a Walpole type of colorimeter against that of a solution in boiled water of 100 to 1000γ of potassium dichromate per c.c.; 1000γ $K_2Cr_2O_7$ per c.c. ≡ 10γ lutein per c.c. Lutein is readily soluble in ether, acetone or chloroform, moderately soluble in carbon disulphide or methyl or ethyl alcohol, and sparingly soluble in petroleum spirit. It decomposes to the extent of 50, 11 and 18 to 20 per cent., respectively, in air at 35° to 40° C., in a vacuum at 19° C., and after standing for 24 hours in the dark in solution in the above-mentioned mixture of solvents, and it is, therefore, important that the period of extraction should be less than 30 minutes. If any foreign colour is present, the usual form of compensation-cell, containing a solution having the same colour, should be added to the colorimeter. The yolks from 6 eggs contained 0·0093 to 0·0186 per cent. of lutein (*i.e.* 1·5 to 2·6 mgrms. per yolk), the error of the method being about ±0·4γ per c.c. for 4 to 13γ of lutein per c.c. Solutions of carotene in the above solvent mixture (1 to 5·5γ per c.c.) are stable for a day, and, when fresh, are equivalent in colour to a solution of lutein about 25 per cent. higher in concentration. J. G.

Characterisation of Aldehydic and Ketonic Sugars by Oxidation with Bromine. F. Zanelli. (*Giorn. Chim. Ind. Appl.*, 1931, **13**, 514–515.)—Precise conditions are given for rendering quantitative the qualitative test proposed by Bertrand (*Compt. rend.*, 1909, **149**, 225) for characterising aldoses and ketoses. A solution of 0·1 to 0·15 grm. of the sugar (previously hydrolysed, if a polysaccharide) in 10 c.c. of water is treated with 25 c.c. of glacial acetic acid containing 10 per cent. of bromine, and kept for 24 hours in a closed vessel in the dark. The bromine is then expelled on a water-bath, and the solution is accurately neutralised with sodium hydroxide. Any residual sugar in the solution is determined by means of Fehling's solution. Under the above conditions, ketonic sugars withstand the oxidising action of the bromine, whereas the aldehyde group of aldehydic sugars is completely oxidised. Results thus obtained with sucrose, raffinose, laevulose, dextrose, galactose, and xylose, are given. T. H. P.

Method of Distinguishing Jams made from Fresh and Dried Plums and their Mixtures. P. Rudolph and H. Barsch. (*Z. Unters. Lebensm.*, **1931**, **62**, **581–582**.)—Kapeller, Praege and Rademeister (*id.*, 1930, **59**, 191) recommend the addition to a filtered 10 per cent. solution of the jam of a tenth of its volume of lead acetate solution, when jams made from fresh plums give a pale or apple-green precipitate, and those from dried plums a brown precipitate. The method is not suitable for mixtures of the two types of jam, and the present authors recommend a method based on the greater enzymic reduction capacity of fresh jams. Ten c.c. of a 10 per cent. filtered solution are maintained for 1 minute at 50° to 60° C. with 1 c.c. of 0·02 *N* iodine solution, and 20 drops of a 1 per cent. solution of starch are then added to the cool mixture. Fresh jams show no reaction (since the iodine is reduced), and dried products give a blue colour. Alternatively, the jam extract may be mixed with 10 drops of a reagent made by dissolving 0·5 grm. of magenta (diamant fuchsin) in 250 c.c. of warm water, adding 12·5 grms. of crystalline sodium sulphite and 7·5 c.c. of 25 per cent. hydrochloric acid, and diluting to 500 c.c. On the addition of 3 drops of 30 per cent. sodium hydroxide solution, jams made from dried plums remain unchanged, whilst jams from fresh plums are coloured red-brown. These reactions are capable of detecting 20 and 10 per cent., respectively, of dried plum jam in fresh plum jams. A brown colour is also obtained with fresh plum jam, but not with dried plum jam, on addition of 30 per cent. sodium hydroxide solution or of 25 per cent. ammonia in the absence of the magenta and sulphurous acid. J. G.

Crystallisation of Honey and the Heating of Crystallised Honey. H. W. de Boer. (*Chem. Weekblad*, 1931, **28**, 682–686.)—According to Gubin (*Archiv für Bienenkunde*, 1926, **7**) all extracted honeys contain small "primary" crystals from which crystallisation of the honey normally originates. Counts of the numbers of these showed that, for a heating period of 1 day, the number is independent of the temperature (− 12° to + 45° C.) at which the honey is stored, but that after 6 to 10 days the number increases with temperature to a maximum at about 10° C., and then decreases; the number for 40° C. is then approximately equal to that for −12° C. The average sizes of the nuclei in microns were 40 (star-shaped), 80 (stars and needles) and 5 (needles only) after 14 days at 0°, 20° and 37° C., respectively. On these and other grounds it is concluded that crystallisation does not originate from Gubin's primary crystals only, but that, on storage, other (secondary) nuclei form at a rate which is a maximum at 5° to 7° C., the maximum rate of actual crystallisation of non-heated honey being at about 15° C. (*vide supra*). Both the rates of formation of nuclei and of crystallisation, therefore, depend on the temperature, the maxima in the two cases being about 10° C. apart. The rate of crystallisation (*V*) may be calculated from the ratio of dextrose to non-sugars, and the values summarised in the table below are in agreement with the behaviour of the samples. The changes in chemical composition which occur on heating were also investigated, and the ratio 100 × fructose to dextrose was shown to increase by 6·2, 0·24 and 1·8 for fruit-tree blossom, rape-seed and for clover and cornflower honeys, respectively, after 6 hours at 70° C. Crystallised honey was also heated in tubes under varying conditions of time and temperature, and curves relating the length of crystalline portion after various heating-periods fall into 2 groups:—(*a*) The length falls rapidly in the first 10 hours and remains unchanged for a further 14 hours (temperature 60° to 80° C.). (*b*) The length rises to a maximum after about 16 to 20 hours, and then falls (45° to 55° C.). Crystallised honey may be rendered fluid by heating (*cf.* Fiehe, *Z.*

Unters. Lebensm., 1926, **52**, 244), but will re-solidify in less than 3 months unless maintained at 60° C. for 4 to 5 hours, or at 65° C. for 2 to 3 hours; below 60° C. even 24 hours' heating will not suffice. The final conclusion is that the decrease in viscosity and sucrose content and the transformation of β- into α-glucose on heating tend to increase V, whilst the corresponding decreases in dextrose content and rate of nuclei formation decrease it.

Honey.	Sucrose. Per Cent.	Dextrose. Per Cent.	Fructose. Per Cent.	Ratio of 100 F:D.	Non-sugars. Per Cent.	*V.*
Rape seed	3·5	36·78	38·78	105·4	1·64	22·4
White clover	1·2	35·97	40·66	113·0	3·38	10·6
Heather	1·7	30·83	41·17	133·5	5·18	5·9
Non-crystallising honey (1)	3·8	33·25	39·8	119·7	6·68	4·9
Non-crystallising honey (2)	2·6	26·19	44·94	171·6	6·77	3·9

J. G.

Simplified Test for the Diastase Content of Honey, and Detection of Foreign Honey by Pollen Analysis. J. Prescher and E. Bohm. (*Z. Unters. Lebensm.*, 1931, **62**, 583–585.)—The authors' experiments (*id.*, 1931, **61**, 504) have shown that in their method (*loc. cit.*) the starch value corresponding with the production of a red colour is, on an average, one-sixth of that corresponding with a blue colour (*i.e.* the diastase value). The test may, therefore, be simplified by adding to 3 separate 5-c.c. portions of 20 per cent. honey solution 1, 2 and 3 c.c. of a 1 per cent. solution of starch. After 1 hour at 40° to 42° C. the solutions are cooled, 3 drops of a 0·02 *N* solution of iodine in potassium iodide solution are added in each case, and the colours are noted. Then 6, multiplied by the limiting number of c.c. of starch solution which give a reddish colour, is the diastase value. If this is 12 or less, Gothe's test (ANALYST, 1916, **41**, 312) should be applied. Identification of the pollen structures in honey from a botanical point of view may often supplement chemical analysis in the determination of the place of origin of a honey (*cf.* Griebel, *Z. Unters. Lebensm.*, 1931, **61**, 275). Examples are given. J. G.

Freezing-Point Depression of Honey. J. Stitz and B. Szigvárt. (*Z. Unters. Lebensm.*, 1931, **62**, 506–509.)—The errors involved in the experimental determination of the freezing-point depression of a solution may be considerably diminished by cooling the solution regularly. The temperature of the cooling mixture used should be not more than 3° C. below the freezing point to be measured, and the stirring of the solution under examination should be regular and not too vigorous. Very energetic stirring results in the introduction of large amounts of air into the solution, and in consequent raising of the freezing-point by 1° to 2° C. Exceptional difficulties are met with in examining solutions of high concentrations, such as honey, which is a supersaturated sugar solution of high viscosity, and has an ill-defined freezing-point. Preliminary dilution of the honey is, therefore, necessary. Measurements of the freezing-points of aqueous solutions of honey of different concentrations show that the normal molecular depression for the solvent (water), *viz.* 1·85° C., is obtained with a 19·71 per cent. solution. The depression is caused almost entirely by the sugars; the ash, protein, acid and other components having very low concentrations. Although dextrose and laevulose are isomeric, they produce different freezing-point depressions at the same concentration, the values for 15 per cent. (by weight) solutions being, respectively, 1·86° and 2·29° C. (sucrose, 1·10° C.). The freezing-point depression for a honey solution of definite concentration must, therefore, depend on the ratio between the percentages of dextrose and laevulose, as well as on that of water in the honey. The depression found for a 15 per cent. solution of a honey is in very close agreement with the sum of the depressions of the three sugars, as given in Landolt and Börnstein's Tables. T. H. P.

Acid Constituents of Wines. II. L. Semichon and M. Flanzy. (*Ann. Falsificat.*, 1931, **24**, 516–534; *cf. Ann. Falsificat.*, 1930, **23**, 5).—The volatile acidity of a wine is taken as the acidity due to fatty acids of the series $C_nH_{2n}O_2$, and may be divided into free and total volatile acidity, excluding acidity due to carbon or sulphur dioxide. In order to be certain that none but volatile fatty acids are being dealt with, it may be necessary to determine any lactic acid, before and after distillation, since proportions of the order of 0·76 to 1·22 per cent. of the lactic acid may be carried over; for this determination the chromic acid oxidation method is recommended, and the acid (expressed as sulphuric acid) is subtracted from the total volatile acidity. To determine the volatile acidity, 50 c.c. of wine are saturated with chalk, concentrated to half the volume, and, after cooling, acidified with a large excess of a concentrated solution of tartaric acid to liberate the free and combined volatile fatty acids. The liquid is filtered after one hour, the residue is washed with four portions of 5 c.c. of boiled water, the filtrates are made up to 50 c.c., and 10 c.c. (corresponding to 10 c.c. of wine) are used for the Blarez distillation method (Blarez, *Vins et Spiritueux*, 1908, p. 131). The carbon dioxide is driven off by boiling on the water-bath. The acidity of the distillate is determined by the author's standard method or by titration with calcium hydroxide solution, using litmus as indicator. If the esterified volatile fatty acids are to be included, the original 50 c.c. of wine, saturated with calcium carbonate, should be heated beneath a reflux condenser for one hour before reducing the volume to one-half. Corrections for sulphurous acid (by titration of sulphur dioxide liberated by sulphuric acid with 0·02 *N* iodine solution) and for salicylic acid (by addition of 1 per cent. ferric ammonium sulphate solution and comparison with standards) are made as necessary. *Formic Acid.*—For this determination, the solution of acids, obtained as above by the Blarez distillation method, is saturated with a slight excess of calcium carbonate and concentrated to 20 c.c., and 5 c.c. of this liquid are added to a cooled mixture of a chromic acid solution (100 grms. per litre) and 5 c.c. of sulphuric acid (1·71 sp. gr.). After 15 to 20 minutes the formic acid is completely oxidised, and the excess of chromic acid is titrated with a solution of ferrous ammonium sulphate. Any lactic acid present will be included as formic acid. *Butyric and Higher Acids.*—These are determined in another 5 c.c. of the wine, which is slowly evaporated to dryness, and 2 c.c. of boiled water and 5 c.c. of the chromic oxidising mixture are then added, drop by drop, the mixture being kept cool. The flask, which is furnished with a long vertical tube to act as condenser, is kept at 55°–60° C. for an hour; under these conditions the butyric and higher acids, together with any lactic acid present, are completely transformed into acetic acid, which is then determined by ferrous ammonium sulphate. *Propionic Acid.*—Five c.c. of the same mixture are dried as described above, the chromic acid reagent is added directly to the residue, drop by drop, with cooling, and the mixture is heated on a boiling water-bath for an hour, when the propionic acid is transformed into acetic acid, as well as the lactic and higher acids, whilst the formic acid is oxidised to carbon dioxide and water. The chromic acid remaining is then determined. *Acetic Acid* is obtained from the difference between the total of the above acids (expressed as acetic), and the total volatile acidity. D. G. H.

Determination of Residual Sugar in Red Wines. J. Dubaquié and G. Debordes. (*Ann. Falsificat.*, 1931, **24**, 477–484.)—Determination by actual fermentation of the residual sugar in a wine as a means of ascertaining the possibility of the wine undergoing after-fermentation is slow, and sometimes gives uncertain results. The cupric reduction method is recommended, use being made of the two solutions: (1) 4 per cent. copper sulphate solution, and (2) a solution containing 20 grms. of Rochelle salt and 15 grms. of carbonate-free sodium hydroxide per 100 c.c. A mixture of 20 c.c. of each of these solutions is boiled for 3 minutes with 10 c.c. of the wine (containing not more than 10 grms. of reducing sugars per litre), the precipitate formed is washed by decantation, and the washings are filtered through an asbestos filter. The cuprous oxide is dissolved in 5 c.c. of dilute (1 : 2) hydrochloric acid, and the solution is treated with 2 c.c. of 10-volume hydrogen peroxide solution, sufficient sodium hydroxide solution to neutralise the 5 c.c. of acid, and 10 c.c. of solution (2). The blue liquid thus obtained represents a Fehling's solution, the sugar equivalent of which is then determined by means of a solution containing 5 grms. of invert sugar per litre. The following table gives, for each 0·1 c.c. of the invert sugar solution between 5 and 15·9 c.c., the reducing sugar content of the wine in grms. per litre.

Invert sugar solution used c.c.	0·0.	0·1.	0·2.	0·3.	0·4.	0·5.	0·6.	0·7.	0·8.	0·9.
5	2·08	2·14	2·19	2·24	2·29	2·34	2·40	2·45	2·51	2·56
6	2·61	2·67	2·72	2·77	2·83	2·88	2·93	2·98	3·04	3·09
7	3·15	3·20	3·26	3·31	3·36	3·42	3·47	3·53	3·58	3·63
8	3·69	3·74	3·80	3·85	3·90	3·96	4·01	4·06	4·12	4·17
9	4·22	4·28	4·33	4·38	4·44	4·49	4·55	4·60	4·66	4·71
10	4·76	4·82	4·87	4·93	4·98	5·03	5·09	5·15	5·20	5·26
11	5·31	5·37	5·42	5·48	5·54	5·59	5·65	5·70	5·76	5·82
12	5·87	5·93	5·99	6·05	6·10	6·16	6·22	6·28	6·33	6·39
13	6·45	6·50	6·56	6·62	6·67	6·73	6·78	6·84	6·89	6·95
14	7·00	7·06	7·12	7·18	7·24	7·30	7·36	7·42	7·48	7·54
15	7·60	7·66	7·72	7·78	7·84	7·90	7·95	8·01	8·07	8·12

T. H. P.

Determination of Lactic Acid in Wines. J. H. Fabre and E. Bremond. (*Ann. Falsificat.*, 1931, **24**, 474–477.)—Möslinger's method of determining lactic acid in wine, as modified by Bonifazi and Ferré (*Ann. Falsificat.*, 1928, **21**, 83), gives results (both with wines and with synthetic solutions similar in composition to wines) accurate to within 0·32 grm. per litre. The procedure is as follows:—Twenty-five c.c. of the wine, in a 150 c.c. flask, are neutralised to phenolphthalein with saturated barium hydroxide solution and treated with 2·5 c.c. of 10 per cent. barium chloride solution. The volume is made up to 40 c.c. with water, and then to 150 c.c. with 96 per cent. (by vol.) alcohol. The whole is mixed, left at rest for 2 hours, and filtered; 100 c.c. of the filtrate are evaporated to dryness in a porcelain dish, and the residue is calcined. The alkalinity of the ash is determined by treatment with 10 c.c. of 0·2 *N* hydrochloric acid and titration with 0·2 *N* sodium hydroxide solution in presence of methyl orange. The result represents the sum of the lactic acid and the volatile acids. The latter may be determined directly by Mathieu's method, even in presence of considerable amounts of lactic acid.

T. H. P.

Determination of Lactic Acid in Wines. A. Michel. (*Ann. Falsificat.*, 1931, **24**, 471–474.)—When applied either to wines or to synthetic media, Bonifazi's method of determining lactic acid gives discordant results. The excess of barium chloride remaining in the filtrate is partly reduced during the subsequent calcination, and thus causes an increase in the alkalinity. With wines rich in potassium salts, these react with the barium chloride, yielding the more stable potassium chloride; for a definite content of lactic acid, such wines give results more accurate than those furnished by wines with less potassium salts. Moreover, it is not easy to neutralise exactly the free acids of the sample, and any excess of baryta, which dissolves readily in alcohol, renders the result too high. It is sometimes assumed that wine may contain dilactic acid, but experiment shows that this acid is very readily hydrolysed and that it does not exist in wine in any appreciable amount.

The following modification of Bonifazi's procedure is suggested:—Twenty c.c. of the wine, rendered alkaline to phenolphthalein with a slight excess of saturated baryta solution, are treated, in a 110 c.c. flask, with 2 c.c. of 10 per cent. barium chloride solution and with sufficient 95 per cent. (by vol.) alcohol to bring the volume to about 100 c.c. The reaction is adjusted, if necessary, to a pink colour, and the liquid is made up to the mark. After being mixed, the liquid is left at rest for 3 hours, in order that the barium succinate may be completely precipitated. The precipitate is removed by centrifuging or filtering, and the liquid is freed from the excess of baryta by means of a current of carbon dioxide or air. When it has settled, the barium carbonate is removed. From 80 c.c. of the remaining liquid, placed in a porcelain basin, the alcohol is carefully expelled on a water-bath; 2 c.c. of approximately *N* potassium sulphate solution are then added, and the evaporation is continued to dryness. The residue is calcined, and the alkalinity of the ash is determined by titration, using 0·2 *N* hydrochloric acid and 0·2 *N* sodium hydroxide. The volatile acids are determined separately, and their amount is subtracted from that of the acids, calculated from the result of the above titration, to obtain the lactic acid. Results obtained with a number of different wines are given.

T. H. P.

Fractional Titration of Wine Vinegar. Determination of Non-Volatile Acids. P. Hirsch and O. Delp. (*Z. Unters. Lebensm.*, 1931, **62**, 589–593.)—The sample (50 c.c.) is steam-distilled with 2 c.c. of 25 per cent. hydrochloric acid until about 600 c.c. of distillate have been obtained, and the residue (about 50 c.c.) is filtered and diluted to 100 c.c. with the washings. Half of this is neutralised, firstly with 2 *N* and then with 0·1 *N* sodium hydroxide solution to phenolphthalein (*p*H 8·3), and transferred to a titration-colorimeter vessel (15·5 cm. × 3·5 cm.), provided with a compensating cell for the elimination of any colour originally present. The liquid is then titrated from *p*H 8·3 to *p*H 2·0 (*r* c.c.) with 0·25 *N* hydrochloric acid in the presence of 0·6 c.c. of a solution containing 100 mgrms. of thymol blue and 4·3 c.c. of 0·5 *N* sodium hydroxide solution per 100 c.c., the end-point being ascertained by comparison of the colour with that of a citrate buffer (Sörensen) of *p*H 2·0 containing, at the end of the titration, the same concentration of indicator as the sample. The influence of "free" acidity (*s* c.c.) is eliminated by a blank titration in the same way with 50 c.c. of water, and the required titration, corresponding with the sum of the tartaric, malic, lactic and succinic acids, is then given by $r - s$ (*cf.* Hirsch and Richter, *id.*, 1929, **58**, 439). Pure wine vinegars (9) contained 22·0 to 27·2 c.c. of 0·25 *N* non-volatile acids per 100 c.c. of sample; a "double" wine-vinegar (50 per cent. blend), 16·4; ordinary vinegar, 20 per cent. blend (6), 4·5 to 5·9; spirit vinegar (8), 0 to 0·2; 80 per cent. commercial "vinegar-essence" (14), 0 to 0·2; a mixture of pure wine and spirit vinegars (1 : 4), 4·75; and "wine vinegars" as sold (7), 0·7 to 5·6. J. G.

Fatty Acids of Chicken Fat and Other Edible Fats. J. Grossfeld. (*Z. Unters. Lebensm.*, 1931, **62**, 553–566.)—*Determination of lower volatile fatty acids.*—Five grms. of fat are saponified by heating over a naked flame in a 300-c.c. flask with 10 c.c. of glycerin and 2 c.c. of 50 per cent. potassium hydroxide solution, and a solution of the soap in 500 c.c. of water is shaken with 250 c.c. of a solution containing 15 grms. of crystalline magnesium sulphate. The mixture is made up to 1 litre, filtered on the following day, and 400 c.c. of filtrate are distilled in a 500-c.c. flask with 5 c.c. of phosphoric acid (sp. gr. 1·154), the first 300 c.c. of distillate being titrated with 0·1 *N* sodium hydroxide solution, with phenolphthalein as indicator. The amounts of lower fatty acids, calculated as percentage of (1) butyric, (2) caprylic and (3) nonylic acid, respectively, were:—Chicken fat, 0·03, 0·05, 0·06; goose fat, 0·01, 0·16, 0·18; beef fat, 0·11, 0·19, 0·21; mutton fat, 0·11, 0·19, 0·21; lard, 0; horse fat, 0·07, 0·11, 0·12; coconut oil, (1) 6·50, (2) 10·64; butter, (1) 5·56. Other analytical values for chicken fat were:—Saponification value, 195·2; iodine value (Hanus), 69·9 to 78·2; thiocyanogen value, 62·7 (ANALYST, 1929, **54**, 304); n_D^{40}, 1·4165. The lead salt method (*id.*, 1930, **55**, 451) gave the following percentages of solid fatty acids:—Chicken fat, 19·27 to 22·66 ± 1·01 (mean 21·36); goose fat, 27·83; horse fat, 29·30; lard, 38·10; beef fat, 40·73 and 53·05; mutton fat, 54·22; hardened arachis oil, 69·9. Saturated fatty acids higher than stearic acid were not detectable in chicken, goose, beef or mutton fats, or in lard. *Iso*-oleic acid occurs in quantities exceeding 1 per cent. only in beef fat (1 to 1·8 per cent.), in mutton fat (5·35 per cent.), and in hardened arachis oil (25·2 per cent.). In all cases the percentage of palmitic acid, calculated from the saponification value, was found to be higher (by 10 for chicken fat) than that calculated from the molecular weight of the solid fatty acids (*cf. id.*, 1930, **55**, 138; *Z. Unters. Lebensm.*, 1930, **60**, 64), and this is attributed to the presence of fatty acids with molecular weights below that of palmitic acid. The mean percentages of stearic, palmitic (+myristic and lauric), oleic (+vaccenic), and linolic acids (Kaufmann's method, *loc. cit.*), lower volatile acids and unsaponifiable matter, respectively, were:

	Stearic acid. Per Cent.	Palmitic (+myristic and lauric) acid. Per Cent.	Oleic acid +*iso*-oleic (vaccenic) acid. Per Cent.	Linolic acid. Per Cent.	Lower volatile acids. Per Cent.	Unsaponifiable matter. Per Cent.	Glycerol residue. Per Cent.
Chicken fat	7·1	18·4	52·7	17·0	—	0·28	4·4
,, ,,	8·5	17·5	52·2	17·1	0·1	—	4·4
Goose fat ..	10·1	20·0	46·8	18·4	0·2	0·14	4·4
Beef fat ..	41·7	18·5	33·0	2·3	0·0	0·08	4·5
Mutton fat ..	34·7	22·2	30·8	7·3	0·2	0·40	4·5
Lard ..	18·7	26·3	40·4	10·2	—	0·11	4·5
Horse fat ..	9·0	27·3	47·6	11·5	0·1	0·29	4·4

A purchased sample of cubes for the preparation of "chicken broth" contained 12·22 per cent. of fat, mainly hardened arachis oil. The Carr-Price reaction for vitamin *A* (*Biochem. J.*, 1926, **20**, 497; *cf.* Cocking and Price, ANALYST, 1926, **51**, 529) gave with 1 grm. of chicken-fat a light blue colour, turning red and producing eventually dark violet flocks, whilst the other fats gave a dark brown or red-brown colour. The colour of the melted fat may be measured by comparison with solutions of potassium dichromate; the colouring matter is partly bleached by the action of nitrous acid or by exposure for 2 hours to ultra-violet light. The colour of chicken fat matched *N*/80 potassium dichromate solution before, and *N*/1280 after the exposure. Experiments, described in detail, indicated the colouring matter of the fat to be closely related to that of hens' egg yolk.

J. G.

Melting and Solidification Points of Hydrogenated Waxes and Oils and of their Fatty Acids. S. Ueno, G. Inagaki and H. Tsuchikawa. (*J. Soc. Chem. Ind. Japan*, 1931, **34**, 445B.)—Little difference was found between the melting and solidification points of five hardened waxes (type unspecified) with iodine values of 4·0 to 8·5. The m.pt. of their fatty acids, however, was 1 to 2° C. higher than the solidif. pt. Four hardened herring oils (iodine values, 2·9 to 4·3) had m.pts. 55° to 57° C., and solidif. pts. of 50° to 50·6° C. The m.pts. and solidif. pts. of the fatty acids showed little difference at about 54 to 56° and 54 to 55° C., respectively. The m. pt. of a hardened sardine oil of iodine value 2·9 was found to be 55·0° to 56·5° C., whilst the solidif. pt. of its fatty acids was 53·5° C. For another sample, with iodine value 18·0, these values were 51·6° to 52·0° C. and 49·5° C., respectively.

R. F. I.

Fatty Acids and Glycerides of Solid Seed Fats. I. Composition of the Seed Fats of *Allanblackia Stuhlmannii*, *Pentadesma Butyracea*, *Butyrospermum Parkii* (Shea), and *Vateria Indica* (Dhupa). T. P. Hilditch and S. A. Saletore. (*J. Soc. Chem. Ind.*, 1931, **50**, 468–472T.)—The objects of the examination of seed fats are to collect sufficient data to establish ultimately the limits within which specific mixtures of fatty acids are characteristic of botanical families, and to obtain further evidence on their glyceride structure and the even distribution of the component acids through the glyceride molecules. *Allanblackia Stuhlmannii* (from the East African Agricultural Research Station, Amani).—The whole seeds yielded 50 per cent. of fat, having m. pt., 40·0° C.; setting point, 35·5° C.; saponification equivalent, 293·2; iodine value, 39·4; acid value, 8·0; unsaponifiable matter, 0·55 per cent. The mixed fatty acids had the mean molecular weight 280·2; iodine value, 41·4; and setting pt., 59·9° C. The mixed fatty acids were submitted to the usual procedure for the separation of solid and liquid acids and fractionation of the corresponding methyl esters, and were found to have the following composition:—Palmitic, 3·1; stearic, 52·6; oleic, 44·1; and linolic acid, 0·2 per cent.; showing 1·25 mols. of saturated acids per mol. of unsaturated acid in the whole seed fat. Oxidation of the fat with potassium permanganate in acetone solution showed that the fully-saturated glycerides in the original fat did not exceed 1·5 per cent., and that the proportion of palmitic acid in the fully saturated components was much higher than in the fat as a whole. The possible amounts of the various mixed glycerides must lie between mono-oleo-disaturated glycerides 63·5 to 82; di-oleo-mono-saturated glycerides 36·5 to nil; and tri-olein nil to 18 per cent., with probable approximation to the first figures.

Pentadesma Butyracea (from Sierra Leone).—The kernels yielded 41 per cent. of a fat having m. pt., 33·5 to 34° C.; setting point, 35·4° C.; saponification equivalent, 294·7; iodine value, 42·9; acid value, 12·5; and unsaponifiable matter, 0·5 per cent. The mean molecular weight of the fatty acids was 281·6; iodine value, 44·5; and setting point, 57·7° C. The fatty acids were found to consist of palmitic, 5·4; stearic, 46·1; and oleic acid 48·59 per cent., showing 1·1 mol. of saturated acid per mol. of oleic acid. The limiting figures for the glycerides worked out at mono-oleo-disaturated, 50 to 75 per cent.; di-oleo-mono-saturated, 50 to nil; and tri-olein, nil to 25 per cent. The distribution of the fatty acids among the glycerol molecules is very largely, but not wholly, of the "even" character usual in seed fats.

Butyrospermum (Bassia) *Parkii*, Fam. *Sapotaceae* (Shea nuts).—Since the conclusions of Bougault and Schuster (*Compt. rend.*, 1931, **193**, 362) are not in agreement with those of the present paper the experimental data are given in some detail. The refined shea butter had the saponification equivalent 314·2; iodine value, 57·3; acid value, 2·1; unsaponifiable matter, 9·5 per cent.; mean molecular weight of fatty acids and unsaponifiable matter, 293·2; iodine value, 57·2; setting point, 51·0° C. The approximate percentages of fatty acids were: Palmitic, 8·5; stearic, 36; oleic, 50; and linolic, 5·5 per cent. The fat contained about 2 per cent. of fully-saturated glycerides with palmitic and stearic in about equal molecular proportions, and the limits for the glycerides were mono-oleo-disaturated 30·5 to 65; di-oleo-mono saturated 69·5–nil, and linolin nil to 35 per cent. (probably nearer the first figures).

Vateria indica (dhupa kernels), *Dipterocarpaceae* (from Bangalore).—The fat had the saponification equivalent 303·5; iodine value, 42·8; acid value, 8·8; and the mean equivalent of the mixed acids was 286·1; iodine value, 45. The component fatty acids were palmitic, 10; stearic, 39; arachidic, 3; and oleic, 48 per cent. The quantity of fat was not sufficient to allow of investigation of the glyceride structure.

The results of the investigation of the component fatty acids of seed fats by modern methods show:

Family	No. of species examined.	Stearic greater than palmitic.	Stearic less than palmitic.
Guttiferae	4	3	1
Sapotaceae	2	2	0
Dipterocarpaceae ..	2	2	0

The analyses of these fats confirm the "evenly distributed" nature of the fatty acids among the glyceride molecules, and the concentration of the palmitic acid in the fully saturated portions is again noticeable. D. G. H.

Determination of Caffeine in Coffee Decoctions and Coffee Extracts. A. Bonn and Ch. Desgrez. (*Ann. Falsificat.*, 1931, **24**, 546–547.)—The following method for the determination of caffeine in infusions and extracts of coffee (also applicable to the determination of added caffeine in wines) is based on the French (1908) Codex method for the determination of caffeine in extracts of cola. Between 75 and 100 c.c. of the liquid are evaporated almost to dryness, the residue is mixed with 15 grms. of recently calcined magnesia, and, after 1 hour, the mixture is transferred to a dry flask and 125 c.c. of chloroform (dried over copper sulphate) are added, and the flask is counterpoised. The mixture is boiled beneath a reflux condenser for 45 minutes, the counterpoise then checked, the liquid filtered, and the volume of the filtrate is noted. The chloroform is distilled off, and the slightly tinted residue is taken up with a few c.c. of chloroform, and finally with 10 c.c. of 5 per cent. hydrochloric acid. A sufficient quantity of 5 per cent. silicotungstic acid to effect complete precipitation is added (about 25 to 30 drops per 10 mgrms. of hydrated caffeine), the precipitate is dissolved by warming, and, after 24 hours, it will have re-formed in a convenient state for filtration. It is washed with 5 per cent. hydrochloric acid, dried, calcined, and weighed; one grm. of the resulting silicotungstic oxide corresponds with 0·2236 grm. of hydrated caffeine. D. G. H.

Determination and Separation of Saligenin, Salicylic Acid, and Salicylaldehyde. R. Berg, W. Grimmer and A. Müller. (*Chem. Ztg.*, 1931, **55**, 975.)—When an ethereal solution of these three compounds is extracted with a measured excess of standard sodium bicarbonate solution, this dissolves all the salicylic acid as sodium salicylate and also a small quantity of the salicylaldehyde, whilst the whole of the saligenin and most of the aldehyde remain in solution in the ether. The unused excess of bicarbonate may be determined by titration with mineral acid, the small amount of salicylaldehyde present serving as indicator. The aldehyde may then be converted into its oxime, and this precipitated in acetic acid solution buffered with sodium acetate and filtered off. After evaporation of the ether from the residual solution, the saligenin may be determined gravimetrically. The procedure is as follows:

The ethereal solution of the three compounds is shaken repeatedly with measured volumes of 0·05 *N* sodium bicarbonate solution; for 0·15 to 0·2 grm. of salicylic acid, four treatments with 10 c.c.-portions of the bicarbonate solution, followed by three treatments with 5-c.c. portions of water, are sufficient. The final washing water must be coloured yellow immediately by a drop of 0·05 N sodium hydroxide solution; if not, extraction with further quantities of bicarbonate must be carried out. The combined pale-yellow extracts are treated with a measured volume of 0·05 N hydrochloric or sulphuric acid—a few c.c. more than are required to decolorise the liquid. The solution is heated to expel the carbon dioxide completely, cooled, and titrated at once with 0·05 N sodium hydroxide solution (as free from carbon dioxide as possible) until a persistent yellow coloration appears. The remaining ethereal solution is carefully concentrated, and the residue is treated with water containing a few drops of dilute sodium hydroxide solution. After expulsion of the ether by distillation, the faintly alkaline liquid is neutralised, and any turbidity is removed by slight addition of alcohol. The solution (about 20 to 25 c.c.) is transferred quantitatively to a stoppered bottle of about 100 c.c. capacity and heated for 30 to 40 minutes in a water-bath at 45° to 50° C. with a solution of 0·2 grm. of hydroxylamine hydrochloride previously made just pink to phenolphthalein by addition of alkali; the end of the reaction is recognised by complete decolorisation of the yellow solution. The product of the reaction is cooled, acidified, and extracted with ether in a separating funnel, the salicylaldoxime and saligenin being then removed from the ethereal solution by shaking this with three or four 5 c.c. quantities of N sodium hydroxide solution. The combined alkaline solutions are neutralised or made faintly acid with a mineral acid and treated with a solution of 0·3 grm. of sodium acetate (neutral or very slightly alkaline to phenolphthalein) and 3 c.c. of 3 per cent. copper sulphate solution. The micro-crystalline copper-salicylaldoxime compound (sometimes mixed with cuprous salt of the excess of precipitant, resulting from reduction of the hydroxylamine) is collected on a fine-pored filter. The saligen is completely extracted from the filtrate by shaking this with ether, and the ethereal solution is dried over anhydrous sodium sulphate and freed from ether by distillation. The residue is dried in a vacuum, and the resulting pure crystalline saligenin is weighed. T. H. P.

Biochemical

Kinetics of Milk Catalase on Heating. A. I. Burstein and F. S. Frum. (*Z. Unters. Lebensm.*, 1931, **62**, 489–500.)—Morgulis's method for determining the catalytic activity of milk (*J. Biol. Chem.*, 1921, **47**, 341) is improved by controlling the temperature of the mixture of milk and hydrogen peroxide solution by means of a thermometer dipping into the mixture itself and not into the bath surrounding the containing flask. The test is made at 17° C., with 60 c.c. of milk, 18 c.c. of a mixed phosphate buffer solution of pH 6·5, and 15 c.c. of 1 per cent. aqueous hydrogen peroxide solution. The method gives results more accurate than those yielded by the so-called "catalasers" of Lobeck, Funke, and others.

Under the above conditions, fresh, healthy milk with acidity (according to Thörner) not exceeding 20, yields 3·5 to 14·5 c.c. of oxygen. When milk is heated, the catalase undergoes gradual inactivation, this effect being influenced more by the temperature than by the duration of the heating. The acidity of milk exerts a protective influence on the catalase during heating. The enzyme is irrecoverably inactivated at a temperature of 90° to 92° C., maintained for 20 to 30 minutes, but if the enzyme is not completely inactivated, the milk improves in catalytic activity when kept. When tested against a control sample, previously heated at 100° C. for 30 minutes, properly pasteurised milk should exhibit catalytic activity, but should not yield more than 8 c.c. of oxygen shortly after pasteurisation. Absence of catalase indicates that the milk had been heated to 90° to 92° C. at least, whilst evolution of more than 8 c.c. of oxygen shows either that the temperature requisite for sterilisation (60° C. at the minimum) had not been maintained for 30 minutes, or that the milk pasteurised was unsound or not fresh.

If pasteurised milk is kept for a few hours, especially if under non-sterile conditions and at comparatively high temperatures, the catalase content increases and may even surpass the maximum value found with freshly-pasteurised milk. Boiled or properly sterilised milk should develop no catalytic activity when stored under any conditions and for any period. T. H. P.

Influence of Sunlight on Milk. H. R. Whitehead. (*Biochem. J.*, 1931, **25**, 1647–1652.)—The author (*Biochem. J.*, 1930, **24**, 579; ANALYST, 1930, **55**, 594) showed that sunlight caused a decolorisation of methylene blue in milk independently of bacteria, and that the reaction was accompanied by an oxidation of some portion of the milk-fat. Other workers have shown that whole milk exposed to sunlight develops a "cardboard" or tallowy flavour, due to oxidation of the milk-fat. It is probable that the presence of methylene blue in milk exposed to sunlight merely results in a visual indication of the intensity with which the oxidation of the fat is taking place. The author has observed that milk samples, exposed to sunlight with or without methylene blue, develop the tallowy flavour, but neither the tallowy flavour nor the reduction of methylene blue occurs in milk from which the fat has been removed, and, therefore, it is almost certain that the two phenomena are dependent upon a single oxidation-reduction reaction. This reaction has been given a more detailed examination. The potentiometric method of Clark *et al.* (*U.S. Pub. Health Service, Hyg. Lab. Bull.*, 1928, No. 151) was applied. The results show that the oxidation of fat in whole milk under the influence of sunlight causes the development of a reducing potential, which can be detected either by its effect on methylene blue or by measurement electrometrically. The fact that a fall in the E_h value occurs in the absence of methylene blue indicates that the dye is not essential to the reaction, and that there must be some reversible system in milk capable of acting as a hydrogen acceptor. The potential developed is poorly poised and of small capacity; hence, experimental error in the measurement of potentials is great. Heated milk and raw milk give similar results. Separated milk, in many cases, undergoes no change under the influence of sunlight, but some samples show a fall in potential which is not at present satisfactorily explained. When such a fall in potential occurs in separated milk there is a subsequent drift to more positive potentials. This suggests the presence in milk of a slowly acting reversible system which tends to maintain the E_h at a value between +0·2 and +0·3v. Most milk samples, in the absence of influences such as sunlight and bacteria, attain equilibrium with a gold electrode at about this value of E_h. It has not been found possible to reproduce the effect of sunlight by the use of either ultra-violet radiation or radiation from electric lamps. The agent inducing oxidation of fat in milk is probably some portion of visible light of which there is less in the radiation of the mercury vapour lamp than in sunlight. *In certain cases (e.g. whole milk undergoing rapid changes in sunlight) the potential* on the electrode seems to lag in its indication of the conditions in the medium. When the E_h falls more gradually or the medium is more nearly homogeneous, the potential on the electrode gives a more accurate indication of the conditions in the medium from moment to moment. Therefore, under certain conditions, a dye may give a truer indication of the oxidation-reduction potential of a solution than the potential on an electrode. P. H. P.

Method for the Direct Determination of Urea in Urine. S. W. Cole. (*Biochem. J.*, 1931, **25**, 1653–1655.)—A modification of the method of Marshall (*J. Biol. Chem.*, 1913, **14**, 483; ANALYST, 1914, **39**, 39) is described by which the determination of urea in urine can be completed in 20 minutes; it is accurate to within 2 per cent. A stronger enzyme preparation is used, and the fluid is maintained under optimal conditions of reaction. The solutions required are:—(*a*) 0·1 *N* hydrochloric acid, in two burettes; (*b*) mercuric chloride, 0·5 per cent. made up to 100 c.c.; (*c*) ammonium chloride, 10 per cent.; (*d*) phenolphthalein, a saturated solution in 50 per cent. alcohol; (*e*) methyl red, 0·02 per cent. in 60 per cent. alcohol; (*f*) urease solution, made from "Arlco" Jack Bean Meal. Four grms. of the meal are rubbed in a mortar into a cream with 10 c.c. of distilled water, washed into a beaker with more water until 100 c.c. have been added, stirred, left for some minutes, and poured off from the deposit of starch and other insoluble material. This preparation is simply made, but gives a precipitate at the final end-point of the titration, which does not interfere with the accuracy. For an almost clear solution, a 4 per cent. suspension of the meal is made as described above, with the exception that the last 50 c.c. of water are warmed to about 60° C. before being added. The whole is treated with 4 c.c. of 0·1 *N* hydrochloric acid, mixed, and filtered through a pleated paper. The slight precipitate, which is gradually deposited, should not be filtered off. The method of determination is as follows:—To 3 c.c. of filtered urine in each of two similar 100-c.c. beakers, labelled A and B, are added about 20 c.c. of distilled water at 60° C. and 5 drops of the phenolphthalein solution. Then 10 c.c. of the enzyme preparation are added to A. The mixture in A is titrated with 0·1 *N* hydrochloric acid, at such a rate as just to discharge the red colour; this prevents loss of ammonia, and maintains a reaction of about *p*H 8·2. It is not generally necessary to add any acid after about 5 minutes. While A is left standing for about 12 or 15 minutes, 1 c.c. of the mercuric chloride solution and 1 c.c. of the ammonium chloride solution are placed in B, mixed, and 10 c.c. of the enzyme preparation and 20 drops of the methyl red are added. In this case the urease cannot act in the presence of the mercury. From a second burette 0·1 *N* hydrochloric acid is added until a full red colour is obtained, and enough water to make the volume slightly greater than that in A. The fluid in A is then treated with 1 c.c. of the mercuric chloride solution and 20 drops of methyl red, and titrated with hydrochloric acid until the colours of the fluids in the two beakers match, the volumes being kept constant by the addition of water to one or the other. As 1 c.c. of 0·1 *N* hydrochloric acid is equivalent to

3 mgrms. of urea, the number of c.c. of the acid added to A, less that added to B, gives the urea in grms. per litre. P. H. P.

Colorimetric Determination of Uric Acid in Urine. H. B. Salt. *Biochem. J.*, **1931**, **25**, **1720–1723.**)—Although one of the difficulties of the determination of uric acid in blood, namely, the development of turbidity in the final solution used for colorimetric comparison, has been entirely overcome, the method for uric acid in urine has not been studied, so far as is known, with this aim in view. Therefore, the method of Folin (*Laboratory Manual of Biological Chemistry*, **1923**, p. **141**) for the determination of uric acid in urine has now been investigated, and a modification is described, which is easily carried out in routine practice, yields results strictly comparable with those obtained by Folin's original technique, and is free from the objection of turbidity in the final colours. Folin's method depends upon the reduction of phospho-18-tungstic acid by uric acid in the presence of a large excess of sodium carbonate; sodium cyanide is also present, and the reaction proceeds at room temperature. The improved uric acid reagents have been substituted, and the conditions of reaction modified. The following reagents are required for the new method:—(1) Uric acid reagent of Folin and Marenzi (*J. Biol. Chem.*, **1929**, **83**, **109**); (2) uric acid standard solution of Folin (*J. Biol. Chem.*, **1930**, **86**, **179**), containing 1 mgrm. uric acid per c.c. This is diluted ten times with water alone, to prepare the working standard when required; (3) cyanide-urea reagent of Folin (1930); (4) acid silver lactate reagent prepared by the method of Folin (*J. Biol. Chem.*, 1922, **54**, 153; ANALYST, 1922, **47**, 309); the solution is always filtered immediately before use; (5) sodium carbonate solution containing 20 grms. of anhydrous sodium carbonate per 100 c.c. of solution. This is referred to as "20 per cent. sodium carbonate." Suitable dilutions are made, *e.g.* "10 per cent. sodium carbonate" is a 1 : 1 dilution. The method recommended is as follows:—To 1 c.c. of urine (or more if the uric acid content is low) in a centrifuge tube are added 3 c.c. of water and 3 c.c. of acid silver lactate solution. The whole is mixed, left in the dark for a few minutes, and then centrifuged. The supernatant liquid is discarded. The precipitate is dissolved in 5 c.c. of cyanide and urea reagent and transferred quantitatively to a 100 c.c. measuring flask, and two successive portions of 10 c.c. of 10 per cent. sodium carbonate solution, and finally 5 c.c. of water, are added. For the standard, 5 c.c. of standard uric acid solution (containing 0·5 mgrm. of uric acid), 5 c.c. of cyanide and urea reagent and 20 c.c. of 10 per cent. sodium carbonate solution are transferred to a 100-c.c. measuring flask. To each flask are then added 5 c.c. of uric acid reagent, and the contents are mixed, and allowed to stand for 5 minutes. The contents of each are diluted to volume, mixed, and compared in the colorimeter. P. H. P.

Amounts of Aluminium in Plants, especially Edible Plants. G. Bertrand and G. Levy. (*Bull. Soc. Chim.*, **1931**, **49-50**, **1417–1425.**)—Aluminium was found to be present in all the phanerogams examined, varying from a tenth of a mgrm. to several dgrms. per kilo. of dry material, and the results showed that the absorption is most rapid during the early life of plants. Edible cultivated roots appear to contain considerably less aluminium than wild ones (*e.g.* forage beet 6 mgrms. per kilo. of dry material, young carrot 30 mgrms., dandelion 120 mgrms.), and the amounts present in tubers are of the same order as in the edible roots. The same is true of most fruits, but bananas and oranges contain very little aluminium (6–7 mgrms. for oranges, 1·4 mgrm. per kilo. in the edible part of the bananas). Seeds are also poor in aluminium; *e.g.* maize 0·2 mgrm., and white rice 1·4, but coffee contained 46·2 mgrms. per kilo. It is in leaves that the highest proportions are usually met with, *e.g.* rhubarb 166 mgrms., Ceylon tea 465, plantain 60 mgrms. per kilo. Etiolated leaves contain hardly any aluminium; for example, the outside leaves of a cabbage contained 232 mgrms., and those inside 8 mgrms. per kilo. D. G. H.

Vitamin *B* Content of Commercial Liver Extracts and Stomach Preparations. E. Gilroy. (*Lancet*, 1931, **221**, 1093–1098.)—During the past year eleven commercial liver extracts and four stomach preparations, as used in the treatment of pernicious anaemia, have been tested for their ability to promote normal growth in young rats on a diet deficient in all water-soluble vitamins. Nine of the liver extracts and three of the stomach preparations gave excellent growth. (A twelfth liver extract subsequently tested gave good growth.) From certain preliminary experiments it appears that a liver fraction for intravenous injection does not contain vitamin B_1, the antineuritic factor. The equivalent of 16 grms. of fresh liver was found to be an efficient dose; half this amount induced fair, but subnormal, growth. Standardisation of the first extract to be tested showed that 1 c.c. (equivalent to 16 grms. of fresh liver) was approximately equivalent to 1 grm. of acetone-extracted wheat germ. The addition of a fraction soluble in 92 per cent. alcohol (discarded in the process of manufacture) to the two extracts which failed to support normal growth, caused an immediate resumption of rapid growth; however, an alcohol-soluble fraction, rejected from the other extract, failed to have any effect. In the two extracts referred to, the amount of the antineuritic factor was considered to be negligible. Therefore, the conclusion is justified that liver and stomach preparations, as used in the treatment of pernicious anaemia, are rich in vitamins B_1 and B_2, and only in exceptional cases does the process of manufacture exclude the first factor of the complex; it is seldom actually destroyed, as the method of preparation is not liable to cause any inactivation. It is the more remarkable that vitamin B_2 is not destroyed, or, at any rate, partially removed, in the process of manufacture, since this always involves extraction, or washing, with alcohol of a strength which should cause considerable loss of B_2. Differences in *p*H are known to modify the sensitivity of B_2 to alcohol, but it seems unlikely that commercial liver-extract would be a sufficiently acid medium to protect the vitamin completely, and it must be assumed that some other factor is responsible for the survival of vitamin B_2 in proprietary liver extracts. In a small series of experiments upon mice, evidence was obtained that a dose of liver extract sufficient for maintenance in the normal, unmated, adult animal is inadequate during pregnancy. It appears possible that premature births, and other morbid phenomena, may be associated with a relative deficiency of vitamin *B*. The significance of the antineuritic factor of the vitamin *B* complex in the aetiology of certain types of pernicious anaemia, and in the treatment of such conditions, is discussed, with reference to recent clinical observations. It is appreciated that

the "pernicious anaemia" of pregnancy, which has been shown to respond to treatment with marmite, may prove to be distinct from typical Addison's anaemia, and that the latter may prove entirely resistant to similar forms of treatment.
P. H. P.

Colour Reactions of Liver Oil. R. T. A. Mees. (*Chem. Weekblad*, 1931, **28**, 694–696.)—The author objects to the Carr-Price test (*Biochem. J.*, 1926, **20**, 497; *cf.* Cocking and Price, ANALYST, 1926, **56**, 529), principally on the ground that the colour is not sufficiently stable. He found that 5 c.c. of a 10 per cent. solution of antimony trichloride in benzene give a colour with 0·5 c.c. of oil which increases to a maximum after 2 to 3 hours. It is less sensitive than the Carr–Price colour reaction, however, though comparative tests on cod-liver and palm oils gave parallel results for vitamin *A* content by the two methods; for example, when the Carr–Price colours were 13·5 B (blue) and 14 B + 4 Y (yellow), respectively, the new method gave (11·9 B + 12·2 Y) and (2B + 55Y), respectively, the preponderance of yellow in the latter case being due probably to the presence of carotene. Solutions of the reagent in trichloroethylene or carbon tetrachloride gave colours similar to that of the Carr–Price test, though developing less rapidly in the latter case, *e.g.* to (10B + 35Y) with a liver oil having a Carr–Price value of 12·5 B; amyl acetate and chlorobenzene also produced more stable but weaker colorations, whilst with toluene and xylene a greenish tint was obtained. A 20 per cent. solution of aluminium trichloride in ether gave in 15 minutes with the same sample a colour matching 50 red. J. G.

Water Analysis

Titration of the Alkali Metals in Water. J. Tillmans and E. Neu. (*Z. Unters. Lebensm.*, 1931, **62**, 593–596.)—The sample (50 to 1000 c.c., according to the alkali metal content) is evaporated with 10 drops of sulphuric acid in a platinum dish, and the residue is gently ignited to remove organic matter and excess of acid. A boiling solution of the residual sulphates is precipitated with a slight excess of barium hydroxide solution, and the mixture is then cooled, made up to a definite volume and filtered, and carbon dioxide is bubbled through an aliquot portion of the filtrate (containing phenolphthalein) until the red colour has disappeared. The colour is restored by evaporation of the mixture, and the precipitation of the alkaline earth carbonates is completed by addition to the boiling liquid, drop by drop, of exactly 20 c.c. of 0·1 *N* sodium carbonate solution. The mixture is filtered when cold, the precipitate is washed with 25 c.c. of cold water free from carbon dioxide, and the alkali metal carbonates are titrated with 0·1 *N* hydrochloric acid to methyl orange. If allowance is made for the amount of sodium carbonate solution required in the last stage, the titration gives the sum of the equivalents of the sodium and potassium salts present. The result is calculated as sodium chloride, and, if no potassium is present, the error is ± 0·3 mgrm. for 8 to 88 mgrms. of sodium chloride (tested for an "artificial" water containing the usual salts). Satisfactory agreement with the gravimetric method was obtained for natural waters containing 3 to 3570 mgrms. of sodium chloride, and having low potassium chloride contents. J. G.

Organic Analysis

Detection and Determination of Methyl Chloride in Air and Foods. M. J. Martinek and W. C. Marti. (*Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 408–410.)—The most efficient field test for leaks of gas containing methyl chloride is carried out by means of a small alcohol lamp with a cone of copper gauze above the wick. In the presence of organic halides the pale blue flame burns bluish-green. The lower limit of inflammability is 8·1 per cent. by volume of the gas in air, and the test is sensitive to 1 part in 100,000. A combustion method is used for laboratory tests. The gas is passed by suction through a quartz combustion tube heated to 1000° C., and then through a bottle containing silver nitrate. The test is sensitive to about 50 parts of methyl chloride per million parts of air. The combustion method is also used for the quantitative determination. The tube is 4 feet long, with an internal diameter of ½ inch, and is heated electrically. The gas to be analysed is measured from a micro-burette or from a 200-c.c. Thoerner gas-sampling bottle, and passed into a dilution chamber, where it is mixed with dry, halogen-free air, and during the combustion the gases are drawn through the tube at the rate of 0·5 cb. feet per hour; the combustion takes one hour. The gases pass into the absorption solutions through tubes containing sintered glass filters, with pores measuring 100–120 microns (No. G1), which break up the gas into small bubbles. The best absorbent was found to be alkaline sodium arsenite, made by dissolving 0·2 grm. of arsenious oxide in 100 c.c. of a 1·0 per cent. solution of sodium carbonate; of this, 20 c.c. are used in each of the two absorption bottles. After the combustion is complete the bottles are removed, and the contents are washed into a 100-c.c. measuring flask containing 5 c.c. of nitric acid (3:1), 25 c.c. of 0·1 *N* silver nitrate solution are added, and the contents are diluted to 100 c.c. After shaking and allowing the contents of the flask to settle, 25 c.c. of the filtered solution are titrated with 0·05 *N* potassium thiocyanate solution, using a 5-c.c. micro-burette capable of delivering drops of the order of 0·01 c.c., a crystal of ferric ammonium sulphate being used as indicator. The error of determination was ±0·5 per cent. For the determination of methyl chloride in foodstuffs or in biological liquids, the material is heated in a flask over a water-bath, and halogen-free air is drawn through the warmed sample at the rate of ¼ cb. ft. per hour, directly into the combustion tube. The hydrochloric acid or chlorine in the foodstuff is determined by passing the hot air from the tube directly into the arsenite solution.

J. W. B.

New Colour Reaction of Formaldehyde and Ketones with Sodium Nitroprusside and Hydroxylamine. P. Pratesi. (*Giorn. Chim. Ind. Appl.*, 1931, 13, 513.)—Sodium nitroprusside solution (not too dilute) is treated with crystals of a hydroxylamine salt and a few drops of 40 per cent. formaldehyde solution, and the liquid is then made alkaline by addition of approximately 2 *N* sodium hydroxide solution. The first drops of the alkali, which liberate the hydroxylamine, produce a yellow coloration, this disappearing when the liquid is mixed. Further addition of the alkali gives an intense, dark, violet-red colour, which persists for days, but immediately changes to yellow if a large excess of alkali is introduced. If sufficient formaldehyde is present, slight evolution of gas occurs. Aliphatic ketones, such as acetone, methyl-ethyl-ketone, and methyl-propyl-ketone, give a similar, but less stable, coloration. The coloured products of these reactions are precipitated from their aqueous solutions by ethyl alcohol. T. H. P.

Quantitative Determination of Acetone in Mixtures of Other Organic Solvents by means of Hydroxylamine Hydrochloride. M. Krajčinović. (*Chem. Ztg.*, 1931, **55**, 894–895.)—Messinger's iodimetric method for the determination of acetone gives high results in the presence of substances (*e.g.* ethyl alcohol or acetate, or impurities occurring in benzol) which react with iodine in alkaline solutions. The author, therefore, recommends the addition of a known amount of sample (*e.g.* lacquer solvent) to an excess (1 to 2 grms.) of hydroxylamine hydrochloride dissolved in a little water containing 2 drops of methyl orange solution in a 200 c.c. flask, and titration with 0·1 N sodium hydroxide solution of the hydrochloric acid liberated according to the equation, $(CH_3)_2CO + NH_2OH.HCl = (CH_3)_2C{:}NOH + H_2O + HCl$; then, acetone = 0·0058 × c.c. used. Since the reagent decomposes on keeping, especially in the light, it should first be tested for free hydrochloric acid, and neutralised, if necessary. The error for 0·23 to 9 grms. of acetone per 100 grms. in the presence of the above solvents is – 0·5 (with benzol) to +1·2 mgrms. J. G.

Quantitative Analysis of Dyestuffs. S. R. Trotman and T. B. Frearson. (*J. Soc. Dyers and Color.*, 1931, **47**, 344.)—New methods for the quantitative analysis of dyestuffs have been based on their precipitation by solutions of salts of alkaloids. Direct dyestuffs are completely precipitated by salts of quinine, cinchonine, quinidine and strychnine. They may thus be separated from acid dyestuffs, some of which are not so precipitated. The sodium salt of α-naphthalenesulphonic acid may be completely precipitated by adding an excess of cinchonine sulphate. The precipitate has a composition corresponding with the formula $(RSO_3H)_2(C_{19}H_{22}N_2O)_2$. Found:—Sulphur, 6·17; alkaloid, 58·7 per cent. Calculated: Sulphur, 6·37; alkaloid, 58·68 per cent. The alkaloid was determined by treating the salt with alkali and weighing the liberated alkaloid after extraction with chloroform. Chrysophenine, diamine sky blue, many chorazol colours, titan yellow, Congo red, etc., etc., may be determined in a similar manner. Primuline may also be determined by extraction with a mixture of toluene and absolute alcohol. After-treatment of cotton fabric with an alkaloid did not affect its fastness to light and washing. It is suggested, however, that artificial silk stockings treated with quinine acetate might act as a protective against bites by gnats and mosquitos.

Some acid dyestuffs are completely precipitated by alkaloid—alkali blue 5B, neutral red, cardinal red, milling scarlet, etc. Those which require the use of a strong acid are, in many cases, not precipitated, or, if so, the precipitate is soluble in dilute acetic acid, whereas that given by direct dyestuffs is insoluble—acid magenta, croceine scarlet, and some neolan colours.

Method for separating Direct and Acid Dyestuffs.—The dyestuff solution is well diluted, made acid with acetic acid, and heated to boiling. Excess of cinchonine sulphate solution is added, drop by drop, and the precipitate is collected on a

Gooch crucible. The precipitate is dissolved in boiling water, cooled, re-precipitated as before, filtered off, and washed. The combined filtrates, containing all the acid dyestuffs, are acidified with sulphuric acid, and the dyestuffs are deposited on wool. The precipitate is dissolved, the solution is made alkaline, and the direct dyestuffs are deposited on mercerised cotton. Certain acid dyestuffs may be separated from each other by the same technique, *e.g.* polar red is precipitated, whilst erio anthracene blue 3G is not.

This precipitation of dyestuffs enables inorganic sulphates and chlorides to be readily determined in the filtrate by the usual inorganic methods. It is tentatively suggested that basic dyestuffs may be precipitated by silicotungstic acid in the presence of a little hydrochloric acid. The precipitate, which is insoluble even in boiling water, is filtered off, washed, dried, weighed, and ignited. The residue is $SiO_2.12WO_3$, and from its weight the quantity of basic dyestuff may be calculated.

R. F. I.

Detection of Woody Plant Membranes with Phloroglucinol and Hydrochloric Acid. W. Plahl. (*Z. Unters. Lebensm.*, 1931, **62**, 603–606.)—As the result of a number of experiments carried out under different conditions, the following procedure is recommended:—The specimen is freed from fat in the usual way and extracted in warm water or in 50 to 60 per cent. alcohol to dissolve cell-juices; starch need not be removed. The section is then treated with 2 drops of a reagent consisting of equal volumes of a 2·5 per cent. solution of phloroglucinol in 96 per cent. alcohol and an aqueous solution of chloral hydrate (5 : 2), to which mixture 4 per cent. of hydrochloric acid (sp. gr. 1·124 to 1·126) is added. The test is best carried out in a watch-glass, any excess of reagent being removed by a strip of filter-paper before the specimen is transferred to the microscope slide. The colour is visible after 5 minutes; it reaches its maximum after 15 minutes, and is stable for a day.

J. G.

Sandalwood Substitutes. K. A. Chowdhury. (*Indian Forester*, Sept., 1931; *Perf. Ess. Oil Record*, 1931, **22**, 332–333.)—In order to distinguish true sandalwood (*Santalum album*, Linn.) from kalamet wood (*Mansonia Gagei*, Drum.), a detailed examination of each wood is reported. True sandalwood has white sapwood often tinged with yellow, and brownish-grey heartwood streaked with alternate light and dark bands. The wood has the following characteristics:—Oily and smooth; a strong odour; weight per cb. ft. approximately 60 lbs.; moderately hard; almost straight-grained; texture, very fine and even. The growth rings are fairly distinct, marked by bands of denser fibrous tissue (7·14 per inch). The appearance of the pores is shown in Fig. 1, and the rays have an irregular arrangement, as seen tangentially (Fig. 3).

Kalamet wood has dull white sapwood, blackish-grey heartwood; is oily and smooth, with a faint odour, about the same weight as sandalwood, hard to very hard; slightly twisted-grained; texture fine and even. The growth rings are less distinct and are determined by narrow bands of dense fibrous tissue; 12 to 24 per inch. The very small pores, which are just visible with a hand lens, are mostly arranged in groups (Fig. 2), whilst the fine rays show distinct ripple marks on the tangential surfaces (Fig. 3).

D. G. H.

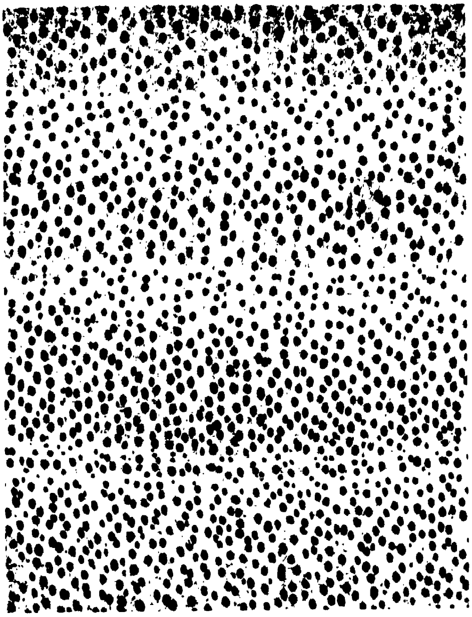


Fig. 1
Sandalwood

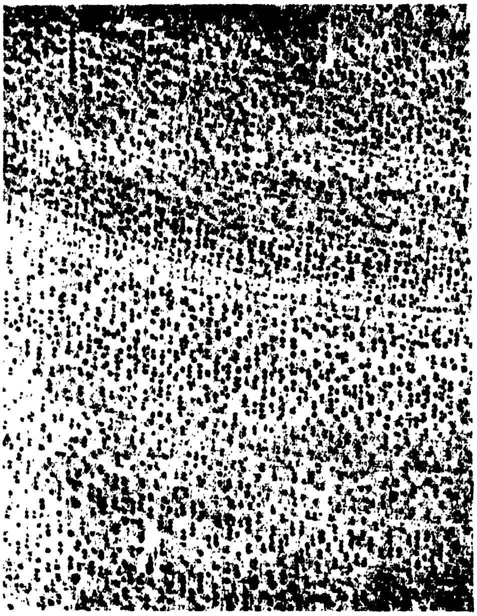


Fig. 2
Kalamet wood

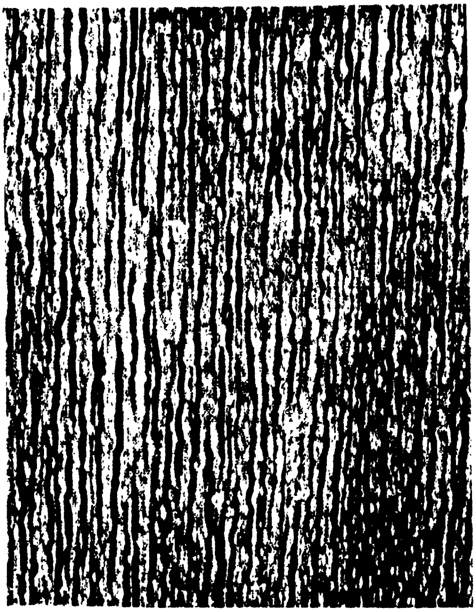


Fig. 3
Sandalwood

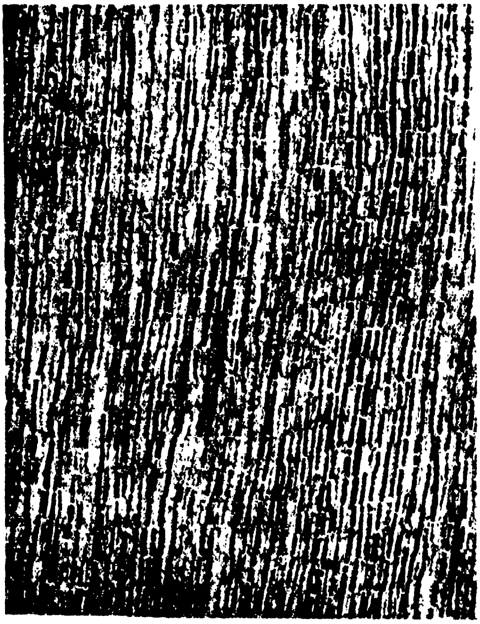


Fig. 4
Kalamet wood

Inorganic Analysis

Volumetric Determination of Iron using Basic Mercuric Bromate. G. F. Smith and H. H. Bliss. (*J. Amer. Chem. Soc.*, 1931, **53**, 4291–4297.)—Ferrous chloride in dilute hydrochloric acid solution is slowly oxidised by bromate at the ordinary temperature, whereas cuprous chloride is rapidly oxidised under similar conditions; the addition of a cupric salt serves as a catalyst in the oxidation of ferrous iron by bromate, since cupric chloride is reduced to cuprous chloride by ferrous chloride. There is a tendency for the cuprous chloride produced to become oxidised by the air before the titration is finished, but it has been found possible to overcome this difficulty by having arsenic acid present, an equivalent amount of which becomes reduced by the cuprous chloride, giving arsenious acid, which, while being unoxidised by the air, is rapidly oxidised by bromate in the cold solution. The following method was adopted for the determination of iron.—To the boiling solution of the ferric iron (containing 10 c.c. of concentrated hydrochloric acid in 25 to 50 c.c.), stannous chloride solution is added, drop by drop, until the yellow colour is discharged, and then one drop in excess. The solution is diluted to 80 c.c., and cooled to room temperature. Ten c.c. of mercuric chloride solution (10 per cent.) are added. Then 10 c.c. of catalyst solution (containing 4 grms. of copper sulphate crystals, 100 grms. of ammonium arsenate, and 500 c.c. of phosphoric acid diluted to 1000 c.c.), and a few drops of fuchsine indicator (strength not stated) are added, and the solution is titrated at room temperature with $N/10$ basic mercuric bromate solution until the indicator is decolourised. The formula of basic mercuric bromate is stated to be $HgOHBrO_3$, but the method of calculating the amount of iron from the amount of bromate solution used is not given; the analytical method does not appear to have been checked against independently known amounts of iron. Certain organic substances, *e.g.* tartaric acid, citric acid, acetic acid, may be present without interference, but formic acid must be absent. It is stated that potassium bromate cannot be substituted for the basic mercuric bromate, since it was found to give slightly low results. The preparation of basic mercuric bromate is not described in the paper (it is given in *J. Amer. Chem. Soc.*, 1924, **46**, 1577); the substance is stated to be now obtainable commercially.

S. G. C.

Separation of Manganese as Peroxide from other Metals. K. A. Jensen. (*Z. anal. Chem.*, 1931, **86**, 422–438.)—A critical study of the persulphate method gave results more or less at variance with those of Majdel (ANALYST, 1930, **55**, 649). In accordance with the experience of other investigators, it was found practically impossible to avoid occlusion of a number of other metals, so that, whilst persulphate precipitation can be used as a step in the volumetric determination of manganese, it cannot pass muster as a precipitant quantitatively separating manganese from all the other common metals. Separation from silver, iron, and cobalt is not feasible. The alkalis are slightly adsorbed; bivalent metals are more or less freely occluded. Thallium, titanium, zirconium, thorium, and the acids of molybdenum, tungsten, and vanadium are co-precipitated. A satisfactory separation by a single precipitation, followed by thorough washing, is possible in the case of the alkalis, beryllium, magnesium, aluminium, and chromium (the latter is oxidised to chromate). Double or treble precipitation (the precipitate being dissolved in sulphurous acid) achieves a quantitative separation from zinc and nickel. If the concentration of the sulphuric acid in the solution is higher than 0·6 *N*, the precipitated peroxide is so finely divided that a turbid filtrate results. The general conclusion is that the process has a certain importance for separations involving the above-named metals, but cannot be used as a general separation procedure. W. R. S.

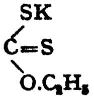
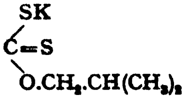
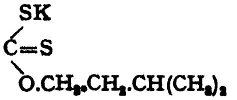
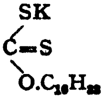
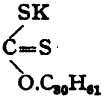
Sensitive Test for Vanadium. F. Ephraim. (*Helv. Chim. Acta*, **1931, 14, 1266–1269.**)—The test, which is stated to have a sensitiveness of 1:400,000, is based on the reaction $V_2O_4 + Fe_2O_3 \rightleftharpoons V_2O_5 + 2FeO$, which takes place from right to left in an acid, but from left to right in an alkaline, medium. The ferrous salt formed is made to react in presence of ammonia with dimethylglyoxime, an intense cherry-red colour being produced. The reduction of vanadate to vanadyl salt is ensured by boiling with hydrochloric acid. One c.c. of solution and one of strong hydrochloric acid are boiled down rapidly to 0·4 c.c. After being cooled in water, the liquid is treated with one drop of fresh 0·1 per cent. ferric chloride, 2 drops of 1 per cent. dimethylglyoxime solution, and excess of strong ammonia: a more or less deep coloration is obtained according to the amount of vanadium present. It is soon bleached unless atmospheric oxidation is prevented by a layer of petroleum spirit. Reduction of the ferric salt by any other substance must be guarded against: no tartaric acid should be present, and the solution should be well cooled before addition of the alcoholic reagent. Chromates also are reduced by hydrochloric acid, though less readily than vanadates; the resulting chromic salt forms a violet ammine compound, though its colour is not strong enough to be taken for the coloration produced by the ferrous compound. W. R. S.

Volumetric Determination of Potassium. Austerweil and Lemay. (*Bull. Soc. Chim.*, 1931, 49, 1541–1542.)—The following process, which occupies about 2½ hours, is advocated.—The test solution is rendered slightly alkaline, and any ammonia present is removed by boiling; it is then acidified with acetic acid (if the test solution contains cyanide or carbonate it must first be acidified with hydrochloric acid and boiled to remove these radicles). The potassium is precipitated as cobaltinitrite by the addition of an excess of sodium cobaltinitrite reagent (a mixture of 800 grms. of 25 per cent. aqueous cobalt nitrate solution, 1 kilo. of 40 per cent. sodium nitrite solution, with 200 grms. of glacial acetic acid, added in small portions at a time); about 40 c.c. of the reagent are required for 0·5 grm. of potassium. The liquid is diluted with one-third of its volume of ethyl alcohol (90 per cent.), heated on a water-bath for about half-an-hour, allowed to cool, and kept for about an hour and a half. The precipitate is filtered off on a sintered-glass crucible and washed with a little water. The crucible is transferred to a porcelain dish, and the precipitate dissolved by heating with 100 c.c. of "dilute" hydrochloric acid. The resulting solution is neutralised with sodium hydroxide, using litmus paper as indicator, and an excess of *N* sodium carbonate solution is added to precipitate the cobalt as carbonate. The liquid is diluted to a known volume, and an aliquot part is filtered off, in which the excess of sodium carbonate is titrated with $N/5$ hydrochloric acid. One c.c. of N sodium carbonate solution = 0·039 grm. of potassium. No test results are cited, but the method is stated to give results accurate to 0·5 to 1·5 per cent. S. G. C.

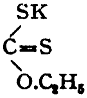
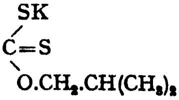
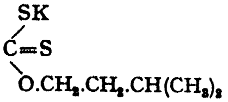
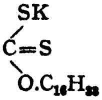
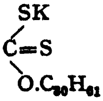
Microchemical

Filter for Micro-gravimetric Analyses. P. L. Kirk and R. Craig. (*Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 345–347.)—The apparatus is suitable for the determination of phosphates, halides and sulphates. Instead of Pregl's method of transferring the precipitate being used, the precipitating vessel is made from a test tube attached to a tapered tube which is ground to fit the filter tube. The stopper of the precipitating tube consists of a hooked glass rod ground in to the tapered tube, which is removed after precipitation, to allow filtration. The filtering surface of the filter tube, which is about 1 cm. from the bottom of the ground-glass connection, consists of a platinum plate, made from foil, 0·005 inch (0·127 mm.) thick, containing small punched holes, 0·5 mm. or less in diameter. This plate is covered with a thin layer of pure washed asbestos. Glycerin is used as a lubricant for the ground-glass connections. Slight suction is used for the filtration. The filter tube is usually weighed alone, but when the precipitate adheres to the side of the precipitating vessel, both may be weighed together; the use of acetone, however, generally prevents the precipitate from sticking. Determinations, with an error of less than ± 2 per cent., were made on varying quantities of the order of 1 mgrm. of chloride and sulphate. The barium sulphate precipitate was not ignited, but dried in Pregl's regenerating block. J. W. B.

Tests using Organic Reagents: Effect on the Sensitiveness of Increasing the Size of the Molecule. J. V. Tamchyna. (*Mikrochem.*, 1931, 9, 229–241.)—Two examples are taken of tests for inorganic ions, using organic reagents, and a number of compounds of increasing molecular weight containing the reactive grouping have been tested. *Copper.*—The formation of yellow copper salts, which is characteristic of all xanthates, is due to the · · O.CS.SH · · grouping. Increasing the molecular weight of the reagent increases the sensitiveness of the test, owing to the decrease in solubility of the resulting compound, but the colour remains the same. The increase in sensitiveness is greatest between ethyl, butyl and amyl xanthate; cetyl and myricyl xanthate are very little more sensitive. The test is carried out on different strengths of copper sulphate, in total volumes of 1 c.c., when 0·1 c.c. of xanthate solution is added, and 5 c.c. when 0·5 c.c. of reagent is added; two drops (0·5 c.c.) of N hydrochloric acid are then added, and, if necessary, the mixture is heated to 70° C. The xanthate reagent is used in a 0·5 per cent. aqueous solution of the potassium salt. Cetyl and myricyl xanthate, since they are too insoluble in water, are used in saturated alcoholic solution, and 0·2 c.c. and 1 c.c. respectively, are added to the test solutions. The sensitiveness of the reaction is shown in the following table:

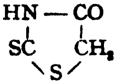
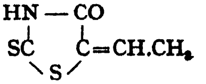
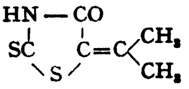
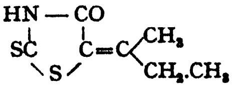
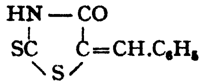
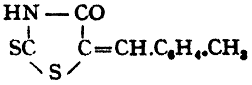
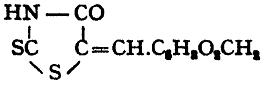
	Reagent.	Smallest amount of copper detectable in 1 c.c. γ	Limit of dilution.	Smallest amount of copper detectable in 5 c.c. γ	Limit of dilution.
1.	 $SK.C(=S).O.C_2H_5$	1·20	1:850,000	5·0	1:1,000,000
2.	 $SK.C(=S).O.CH_2.CH(CH_3)_2$	0·75	1:1,300,000	2·0	1:2,500,000
3.	 $SK.C(=S).O.CH_2.CH_2.CH(CH_3)_2$	0·75	1:1,300,000	1·5	1:3,300,000
4.	 $SK.C(=S).O.C_{16}H_{33}$	0·50	1:2,000,000	1·0	1:5,000,000
5.	 $SK.C(=S).O.C_{30}H_{61}$	0·50	1:2,000,000	1·0	1:5,000,000
6.	Viscose	2·5	1:400,000		

Molybdates.—These also react with potassium xanthate, forming a yellow-red precipitate which rapidly turns violet. The results in the table resemble those obtained with copper. The test was carried out in the same way.

	Reagent.	Smallest amount of molybdate detectable in 1 c.c. γ	Limit of dilution.
1.	 $SK.C(=S).O.C_2H_5$	2·0	1:500,000
2.	 $SK.C(=S).O.CH_2.CH(CH_3)_2$	0·65–0·74	1:1,500,000
3.	 $SK.C(=S).O.CH_2.CH_2.CH(CH_3)_2$	0·5	1:2,000,000
4.	 $SK.C(=S).O.C_{16}H_{33}$	0·5	1:2,000,000
5.	 $SK.C(=S).O.C_{30}H_{61}$	0·5	1:2,000,000

The tests may also be carried out on filter paper, using a drop of test liquid, when the smallest amount recognisable is less than 0·1γ, but the limit of dilution is not so great, 1:500,000.

Silver.—The tests for silver, using rhodanine derivatives, also show that the sensitiveness increases with increase of molecular weight. When a benzene ring is present in the molecule, the colour intensity is greater, and this considerably increases the sensitiveness of the test. The reagents are all used in 0·05 per cent. alcoholic solution. The test solutions are made slightly acid with nitric acid. The colour change is visible in 3 to 5 minutes.

	Reagent.	Smallest amount of silver detectable in 1 c.c. γ	Limit of dilution.
1.		13–14	1:70,000
2.		10	1:100,000
3.		8·4–8·7	1:115,000– 1:120,000
4.		8·4	1:120,000
Phenyl derivatives.			
1.		5 (visible ppt.) 0·4 (colour change)	1:200,000 1:2,500,000
2.		5 (visible ppt.) 0·4 (colour change)	1:200,000 1:2,500,000
3.		5 (visible ppt.) 0·5 (colour change)	1:200,000 1:2,000,000

J. W. B.

Micro-Determination of Sodium in Biological Materials. R. A. McCance and H. L. Shipp. (*Biochem. J.*, 1931, **25**, 1845–1848.)—McCance and Shipp (*Biochem. J.*, 1931, **25**, 449) described a colorimetric method for the micro-determination of sodium (0·02–0·8 mgrm.). The technique is now given for its application:—(*a*) without the necessity for incineration, to blood-serum, milk, cerebro-spinal fluid and urine, and (*b*) to solid tissues, with incineration. *Whole Blood and Serum.*—Trichloroacetic acid is used to precipitate the proteins. To about 8 c.c. of water in a 25 c.c. flask 0·5 c.c. of serum (or 1 c.c. of whole blood) is added, and then with shaking 1 c.c. of 30 per cent. trichloroacetic acid (or 3 c.c. in the case of whole blood). This is left for 5 minutes, made up to the mark, mixed, and filtered through an ash-free paper; 1 c.c. of the filtrate is taken for each sodium determination, which is carried out as previously described. In whole blood determinations ammonium oxalate is used in place of lithium oxalate as an anticoagulant. *Cerebrospinal fluid.*—The technique is exactly the same as for blood-serum. *Urine.*—In urine there is usually enough sodium available to enable macro-methods to be used, but for investigations on small experimental animals or even insects a micro-method is desirable. An accurate 1 in 25 or 50 dilution of the urine is prepared, and 1–2 c.c. of this diluted urine are taken and treated as described previously. *Milk.*—Bromine is used as the protein precipitant. Five c.c. of milk are placed in a 50 c.c.-flask, and diluted to about 15 or 20 c.c. with distilled water; 10 c.c. of saturated bromine water (for human milk) or 15 c.c. (for cow's milk) are then added, and, after shaking, the volume is made up to 50 c.c., and the suspension is filtered through an ash-free paper. For each determination 1 to 1·5 c.c. of the filtrate (which should be yellow) is taken, the phosphates are removed with zinc acetate in 50 per cent. alcohol, and the sodium is determined, as usual, by precipitation with uranyl zinc acetate. *Solid tissues.*—The method is applied to hydrochloric acid extracts of incinerated material. An inexpensive incineration apparatus, to take the place of an electric muffle furnace with graduated resistance, is described. Tables show the results obtained by the new method for body fluids compared with an incineration method, and the recoveries of known amounts of sodium added to various body fluids. P. H. P.

Physical Methods, Apparatus, etc.

New Micro Melting-Point Apparatus. L. Kofler and H. Hilbck. (*Mikrochem.*, 1931, 9, 38–44.)—An electric heating plate is described for observing melting points or sublimation under the microscope. It is similar to Klein's apparatus (*Mikrochem. Pregl-Festschrift*, 1929, 192), except that the temperature is measured by means of a thermo-couple, instead of a thermometer imbedded in the copper heating block. The authors found errors of 4° to 8° C. when using Klein's apparatus at high temperatures, but, with a heating plate with the temperature measured (using a copper-Constantin element) the maximum error was reduced to ± 1° C. up to 200° C., and to ± 2° C. between 200° and 300° C., when for the final 10° before the melting point the temperature was not allowed to rise more than 1° to 2° per minute. The apparatus is suitable for magnifications up to 135 diameters. J. W. B.

Simple Fluorescence Microscopy and Fluorescence Photomicrography. P. Metzner. (*Mikrochem.*, 1931, 9, 72–91.)—A parabolic mirror (Busch) is described, made of a metal which strongly reflects ultra-violet light, for attachment to the microscope in observing fluorescence phenomena in incident light. The mirror focuses the ultra-violet light on to the object to be observed, and renders sufficient the illumination obtained from an ordinary quartz or mercury lamp. The illumination can be still further increased by interposing a round glass flask filled with distilled water, as a focusing lens, between the lamp and the black ultra-violet light-filter, and so adjusted that the image of the lamp falls on the mirror. This is better than a large lens, which would absorb some ultra-violet light. When an arc lamp is used, nickel is preferable to carbon, as it emits more ultra-violet light. The condenser lens of the arc lamp, which may be of ordinary glass (though Uviol glass is better) is adjusted to give almost parallel light which falls horizontally on the parabolic mirror. An ultra-violet light-filter is placed between the lamp and the microscope, and, to absorb red rays the beam is passed through a half-saturated solution of copper sulphate in a container made of two thin-walled glass plates held together by a thick rubber ring, in which are two holes for filling. The illumination by means of the parabolic mirror is suitable for use with low-power objectives (up to Leitz 5). For photographic purposes it is necessary to use a "Euphos" cover-glass (Zeiss), or an ultra-violet light-filter to cut out any ultra-violet light that may be reflected. A number of photographs were taken of plant material in a non-fluorescing medium (water or glycerin). The time of exposure varied from 20 to 60 minutes.

J. W. B.

Fluorescence Microscopy with Strong Illumination. M. Haitinger. (*Mikrochem.*, 1931, 9, 430–440.)—Faintly fluorescing substances, such as the chlorophyll in algae, are not sufficiently illuminated by mercury lamps or carbon arc lamps for microscopy. Brighter illumination is given by an arc lamp with iron as the electrode metal. Iron is the most suitable element, as it emits light a large percentage of which has wave-lengths between 3000 and 4000 Å.U. To maintain evenness of illumination and to prevent poisoning of the electrodes by formation of iron oxide, the electrodes are as short as possible, and imbedded in coolers of ribbed brass; they are also bored and filled with brass. With a direct current of 5 ampères the arc glows with sufficient regularity for hours. The light from the arc passes through a convergent lens of quartz or glass non-absorbent of ultra-violet light, then through a dark glass ultra-violet light-filter and a solution of copper sulphate, to absorb red rays, before being directed on to the mirror of the microscope. The loss of ultra-violet light on a silvered glass mirror, when the glass does not absorb ultra-violet light, is negligible. However, iron plated with chromium may also be used as a mirror. The light passes through a dark ground condenser of quartz, or glass which does not absorb ultra-violet light, on to the object. To prevent any ultra-violet light coming through to the eyes or photographic plate a stopping filter must be used; this cuts off the light between 3000 and 4000 Å.U. As the illumination is very bright, short exposures of a few minutes are sufficient for photographing the fluorescence. The apparatus is suitable for work at any magnification; for high powers the microscope is used horizontally and the mirror dispensed with, to avoid the slight loss of light. The dark-glass filter can be rapidly replaced by an opal glass filter for comparison with the appearance of the object in ordinary light. When non-transparent objects are viewed, incident light must be used; this is achieved by means of a periscope of two mirrors.

J. W. B.

Reviews

The Vitamins. By Ethel Browning, M.D. (Liverpool). Pp. 575+xxxii. London: Baillière, Tindall & Cox. 1931. Price 42s.

This is much the largest book yet published about vitamins in English, or, indeed, as far as I know, in any language. The amount of labour that must have gone to its compilation is so enormous that the voice of criticism is almost drowned by the cheer of admiration. It contains, besides the text and a bibliography of at least 3000 references, 45 pages of tables showing the Vitamin Content of Foodstuffs, a number of diagrams and illustrations, 7 plates, and indexes of authors and subjects.

In Part II there is a discussion of vitamins in general; subsequent parts treat in detail of each known vitamin separately. The arrangement of the sub-sections under the heads of the individual vitamins is thorough and systematic. The author has deliberately emphasised the clinical aspect of the subject, and in so doing, has assembled much scattered information not previously obtainable without an exacting amount of search in the literature.

The body of the book consists mainly of a summary of published papers; it contains nothing in the way of commentary upon them. It is clear, from internal evidence, that the author has certainly read the "conclusions" of all these papers, not merely abstracts of them, and in many cases the papers themselves. The number of papers summarised appears to be of the same huge order as the number of references in the bibliography.

At the end of the book, after an Addendum of 10 pages, containing "information brought to the notice of the author too late to be incorporated in the general body of the text," is a section entitled "Author's Summary and Conclusions," occupying 22 pages, and constituting the only critical part of the book. Even here, however, it is the summary rather than the conclusions that receive emphasis, so that the book must be regarded almost solely as a book of reference.

Its nature is, therefore, such as to justify a demand for scrupulous accuracy in the record of the work done in vitamin research during the past twenty years. It is impossible fully to establish whether this demand is met, since it would take even longer to check all the statements made in the book than it must have taken to write it. One can at most indulge in some "random sampling," only selecting in so far as to choose the summaries of work with which one is best acquainted.

From such a test the book does not emerge unscathed. The first sentence at the top of p. 13 is quite incorrect (as is clear from statements later in the book): the "P.P." factor is not necessary for the normal growth of pigeons. On p. 133 it is stated that vitamin *D* forms an insoluble digitonide, and is destroyed by treatment with bromide. The second statement is probably due to a misprint; the first is quite untrue. Instances could also be given of chemical formulae and equations that are wrong, misleading or meaningless, and of the consistent mis-spelling of authors' names.

In general, the author is least useful when she is summarising the more definitely chemical aspects of the subject. In view of the existence of Sherman and Smith's excellent monograph (reviewed by K. H. Coward in the ANALYST, 1931, 56, 491), it would probably have been better to have rigorously restricted the treatment of those aspects, and to have laid more emphasis, and applied actual criticism to, the clinical aspects with which the author is so obviously more familiar. However, that would, in practice, have meant writing a different book from the one she has actually written and presumably intended to write, and, though such a book is still needed, a reviewer is mainly concerned with noting how far an author has carried out his avowed object, and the comment must be regarded rather as an *obiter dictum* than as fair criticism. It cannot for a moment be denied that this almost monumental volume has great value as a repository of present-day knowledge about vitamins.

Unfortunately, the utility of the book has been unforgiveably limited by the publisher's parsimony. The volume measures 11×8½×2 inches, and weighs a shade under 4 lbs. It is a book that will certainly be used mainly as a reference book, and will therefore be handled for short periods, but repeatedly. Its price means that few will buy it who do not definitely need it—that is the almost inevitable fate of *biblia abiblia*, especially if they have over 600 pages. Had its price been a few shillings more, its circulation would probably have been unaffected. So that even considerations of economy do not really afford the least justification for the fact that it is published—*in paper covers!* A. L. BACHARACH.

COLLOID ASPECTS OF FOOD CHEMISTRY AND TECHNOLOGY. By WILLIAM CLAYTON, D.Sc., F.I.C. Pp. vii+571; with 64 illustrations. London: J. & A. Churchill. 1932. Price 36s.

As a sign of the fundamental changes which have occurred in the chemical industrial outlook during the last twenty or thirty years, one has only to compare the scope and character of an industrial text-book of that date with those of a work such as the one which has just come from Dr. Clayton's pen. In the earlier days the treatment of a subject was, in the main, descriptive, stress being usually laid upon procedure which was inevitably empirical, and, what was even more significant, without any apparent realisation of the essential superficiality and lack of correlation inherent in such a treatment. A compilation of this older type recorded current practice, but was, on the whole, incapable of suggesting new lines of investigation which it would be worth while to pursue, for the very good reason that investigation was considered as something so remote from practice that it was unlikely to possess any direct, *i.e.* economic, value.

That the present attitude is very different is readily demonstrated by an examination of a work such as that before us. It is written for, and intended to be read with profit by, those directly concerned with industrial processes. It is, therefore, significant that the author has obviously no hesitation in giving considerable space to those principles of a purely scientific character which he clearly regards as the only means available wherewith to attack the specific problems which food technology presents.

As is to be expected in a work planned and developed along these lines, the whole subject is seen to bristle with problems inviting further research. The presentation is attractive and can scarcely fail to arouse in others something at least of the enthusiasm which the author himself so evidently possesses.

The precise object which the author has had in view is best described in his own words:—"It is not a treatise on food technology, but rather an introductory guide to those aspects and problems of a colloid nature which may be unfamiliar to the food chemist who has not specialised in colloid chemistry and physics."

A general idea of the scope of the work will be gathered to some extent from the chapter titles, which are as follows:—Agar-agar and gums (with particular reference to swelling under different conditions and the electro-viscous behaviour as worked out in Kruyt's laboratory); the colloidal behaviour of proteins (a vast subject excellently epitomised); a special chapter on gelatin (including its use as an emulsifying agent, its behaviour in respect of swelling, capillary activity, viscosity, the problem of turbidity of gelatin solutions, the setting of gelatin and the structure of the gel); the colloid chemistry of the starches, flour and its protein constituents (the strength of flour, the colloidal behaviour of dough and the staling of bread); the properties of emulsions and the theories of emulsification (as applied to butter, margarine, salad dressings, medicinal emulsions and the rôle of emulsions in bread-making); milk and milk products (including the problem of the stability of such systems, the principles underlying churning, homogenisation, coagulation by rennin, cheese and ice-cream); colloid aspects of nutritional chemistry; colloid problems in sugar technology (including molasses, caramel, honey, with the decolorising and other adsorptive processes operative in such systems); fruits, jams, jellies and marmalades (including the fundamental pectin-sugar-acid equilibrium); colloid phenomena in brewing (including, among other topics, the change in the electric charge exhibited by yeast, the surface tension of beer as a function of *p*H and the problem of frothing, beer haze and the Ramsden phenomenon, and the fining of wine); the freezing and thawing of colloid systems (with special reference to the preservation of foodstuffs, the account being based, in the main, upon the remarkable series of researches initiated by Sir W. B. Hardy on behalf of the Food Investigation Board at Cambridge); and, finally, the treatment of water and factory effluents.

In addition, there is included an extensive bibliography, occupying approximately 100 pages, divided into sections for convenience in reference. This, of itself, is evidence of the labour and enthusiasm which the author has brought to bear in order to make the work as complete as possible.

It is obvious that no single reviewer is competent to assess the value of a work which covers such a wide field. The best that one can do is to examine in particular those sections with which one has some degree of familiarity, and to form a judgment on that basis. Examining it in this way, the present reviewer has no hesitation in strongly recommending the book as an eminently successful effort to co-ordinate and correlate apparently very diverse procedures in systems which, at first sight, might appear to have little in common.

The author has had a wide experience in the field of colloids, more particularly as applied to the food industries. It is not surprising, therefore, that the present work emphasises the vital part which scientific principles—in this case the principles of colloid physics and chemistry—play in the development of these industries. For this reason Dr. Clayton's book is indispensable to all engaged, not only in the industries referred to, but in all other branches of chemical industry in which colloids play a part.

W. C. M. Lewis.

FORENSIC CHEMISTRY AND SCIENTIFIC CRIMINAL INVESTIGATION. By A. LUCAS, O.B.E., F.I.C. Pp. 324. London: Edward Arnold & Co. 1931. Price 18s. net.

The term "medico-legal" is still too often loosely used to describe work which is essentially of a chemical nature, and the author of this book rightly lays stress upon the point that there is no justification for a statement such as the following from a work on circumstantial evidence: "One of the most valuable functions of the medical profession is the detection of poison, blood and other matters by chemical examination." The true scope of forensic medicine is distinct from that of forensic chemistry, which, however, now embraces such subjects as the examination of counterfeit coins, documents, stains, etc., which are only partly chemical, and involve the use of the microscope and of physical methods.

Ten years have passed since this book was first published and was reviewed in THE ANALYST (1921, **46**, 529), and in the interval so many advances have been made in nearly every branch of scientific criminal investigation that the author has done well to emphasise this aspect of his work in a sub-title. The excellent plan of arranging the various sections in alphabetical order has been retained; it adds much to the value of the book as a work of reference. Some of the sections have been condensed and others re-arranged or amalgamated; the section on "Stains and Marks," for instance, has been incorporated with "Dust and Dirt," and "Hashish" is now included among the poisons. But even after these changes the size of the book has been increased by fifty-six pages. The section on "Bloodstains" has been entirely re-written, and now includes a concise description of the determination and significance of blood groups. There is also much new matter in the sections on "Explosions and Explosives" and on "Firearms, Cartridges and Projectiles," which now have a scientific literature of their own.

The section on "Poisons" has been completely revised, and includes many additional poisons, such as carbon monoxide, chloral and chloroform, as well as a method for the isolation of veronal from viscera.

Among the important additions to the section on "Documents" are methods for the examination of burnt documents and tests for sizing materials on paper, and the use of fluorescence tests is discussed under this heading, as well as under "Microscopy, Photography and Ultra-Violet Rays," and under "Robbery from Letters and Parcels."

As the Introduction is essentially a valuable summary of the whole practice of forensic chemistry, it will not be out of place to refer to it last. It gives concisely the rules to be observed when receiving exhibits, and deals with their examination, with the writing of reports, and with the presentation of evidence in Court. The author's caution that it is essential to define the exact sense of such terms as "a small amount" or "a trace" will be endorsed by everyone who has tried to get concise definitions of those quantities from a number of chemists. A word of warning, perhaps, is necessary in connection with the author's advice (p. 16) to put a distinguishing mark upon a document. Unfortunately, this practice does not always commend itself to a judge, for as recently as last November Mr. Justice Swift, in the case of *Riddle and Holder* v. *The Midland Bank, Ltd.*, emphatically laid down the dictum that in no circumstances should any mark whatsoever be made upon a document which was to be produced in evidence.

Space does not allow of more than a brief outline of the contents of this work, but sufficient has been said to show how wide is its scope. Mr. Lucas has had exceptional opportunities of applying scientific methods to criminal investigation, and has made full use of them, with the result that his book has a unique position as a work of reference. Every chemist in a consulting practice is at times confronted with out-of-the-way problems involving the identification of materials, and here he will usually find the solution, together with copious references to previous work on the subject. This edition fully maintains the reputation which the author won with its predecessor. EDITOR.

THE MICROSCOPICAL EXAMINATION OF CATTLE FOODS. By S. T. PARKINSON, B.Sc., and W. L. FIELDING, B.Sc., Agric., Dip. Agric. Pp. viii+97. Illustrated with 15 plates, comprising 125 original photographs. Headley Brothers, The Invicta Press, Ashford, Kent, and 18, Devonshire Street, E.C.2. 1930. Price 6s. 6d. net.

The present volume gives a detailed description and pictorial representation of the microscopical appearance of cattle foods, in a form which can be highly recommended to students and also to chemists engaged in the analysis of these articles. The introductory part describes in a practical way the preliminary physical and chemical tests which should be applied in the macro-examination of a cattle food, and, also, the use of the microscope, sources of illumination, and methods of sketching the fragments and making permanent preparations.

The principal food plants are divided into three groups: oil-containing plants, cereals and leguminous plants. Each plant is described separately, and the authors have given an analytical value to the treatment of each group by cross-references in the descriptions to similarities and differences between the various plants, but especially by means of folded pull-out sheets which describe, in condensed tabular form, the macroscopic character and the microscopic appearance of related layers of tissues in each plant of the group.

A microscopist with his finger continually on the fine adjustment can see the forms of thick tissues which are very difficult to reproduce in a photograph, and it is debatable whether sketches or photographs are more suitable for portraying such tissues. The authors have been generally successful in obtaining clear photographs of the tissues, though an exception must be noted in the case of the rice husk picture, which fails to show the wavy character of the cells. A consistent use of one letter to denote the same layer in the different pictures assists comparison.

Miscellaneous constituents of cattle foods, such as sphagnum, cacao shells and weed seeds, are described in a final part, in which the pictures are confined to slightly magnified photographs of the unbroken small seeds, to assist in their macroscopic detection.

Two omissions have been noted. There is no reference to fish or meat tissues, which are frequent constituents of mixed foods, and the meaning of the term μ, used as a dimension in measuring microscopic objects, is not explained.

The volume closes with a bibliography of related works and a very good index. It is bound in a useful form which allows the pages to lie flat on a work-bench, and the price is reasonable. It will be a useful book of reference and textbook for agricultural chemists and students. A. MORE.

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, February 3rd, the President, Dr. J. T. Dunn, being in the chair.

Certificates were read for the first time in favour of:—Alan Arthur Douglas Comrie, B.Sc., A.I.C., Edwin William Stanley Press, B.Sc., A.I.C., and Muriel Roberts, B.Sc., F.I.C.

Certificates were read for the second time in favour of Albert Green, M.C., M.Sc., Ph.D., F.I.C., John Farrar Hardwick, B.Sc., A.I.C., Ernest Stephen Hawkins, B.Sc., A.R.C.S., F.I.C., Joseph Robert Johnson, F.I.C., M.Inst.M.M., Arthur Pillans Laurie, M.A., D.Sc., F.R.S.E., and John Morgan Tucker, B.Sc., A.I.C.

The following were elected Members of the Society:—Thomas Whittaker Lovett and William Charles Wise, B.Sc.

Notice was given that the Annual General Meeting of the Society would be held on Friday, March 4th, at 3 p.m., instead of on Wednesday, March 2nd, and the Anniversary Dinner at 7.30 p.m., on March 4th, at the Trocadero Restaurant.

The following papers were read and discussed:—"A New Method for the Determination of Lead in Organic Substances, with Special Reference to Dyestuffs," by N. L. Allport, A.I.C., and G. H. Skrimshire; "(i) Some Analytical Applications of Sodium Hydrosulphite, II.," and "(ii) A Rapid Method of Dissolving Lead Alloys Preparatory to the Determination of Tin and Antimony," by B. S. Evans, M.C., Ph.D., F.I.C.; "The Phloroglucinol Method for the Determination of Mechanical Wood Pulp in Paper," by H. B. Dunnicliff, M.A., D.Sc., F.I.C., and H. D. Suri, M.Sc.; "Investigations relating to Milk Standards under the Burma Food and Drugs Act," by E. H. Bunce, F.I.C.

NORTH OF ENGLAND SECTION

The Seventh Annual General Meeting of the Section was held in Manchester on February 13th, 1932. The attendance was thirty-two, and, in the absence of the Chairman, Dr. Dunn presided.

The Secretary read the report and the financial statement for 1931, which were adopted.

The following appointments were made:

Chairman: John Evans. *Vice-Chairman:* Prof. W. H. Roberts. *Committee:* J. W. Haigh Johnson, J. Haslam, H. Heap, S. E. Melling, H. E. Monk, and J. Wood. *Honorary Auditors:* U. A. Coates and W. Marshall. *Honorary Secretary:* J. R. Stubbs.

The following paper was read and discussed:—"Castor Seeds in Feeding Stuffs," by F. Robertson Dodd, F.I.C.

The Calcium Fluoride Method for the Determination of Fluoride, with Special Reference to the Analysis of Nickel-Plating Solutions*

BY S. G. CLARKE, PH.D., A.I.C., AND W. N. BRADSHAW, B.Sc.

ONE type of modern nickel-plating solution contains a high concentration of nickel sulphate, together with additions of potassium or sodium chloride to maintain anode efficiency, and of potassium or sodium fluoride and boric acid to act as buffering agents. The solution may also contain small quantities of iron, etc., as impurities. No difficulties arise in the determination of the nickel, sulphate, etc., and the problem of the determination of the borate in this type of solution has recently been satisfactorily solved by Willard and Ashworth (*Amer. Electroplaters' Soc. Monthly Review*, August, 1929, p. 7). A process for the determination of the fluoride has been published (Hammond, *J. Ind. Eng. Chem.*, 1924, **16**, 938), in which the lead chlorofluoride precipitation method is employed; the method is not easy to carry out, and has, in our hands, given a distinctly incomplete recovery of the fluoride. In a search for a suitable method we investigated the possibilities of the calcium fluoride precipitation method, and we have found how this can be used to provide a reasonably rapid and accurate method for the determination of the fluoride in these nickel-plating solutions. Our work further shows how, in the absence of interfering substances, the traditional calcium fluoride process can be simplified and rendered more rapid and accurate.

The calcium fluoride method continues to occupy a prominent position in textbooks since it has fewer disadvantages than other methods for the determination of fluoride. In a modification of this method, by Rose (*Ann.*, 1849, **72**, 343), some calcium carbonate is made to precipitate with the calcium fluoride, with the object of rendering the precipitate less difficult to filter. It is clear that this procedure restricts the method to solutions from which heavy metals, *e.g.* nickel, have been removed. Moreover, the addition of sodium carbonate, which is recommended for producing the precipitate of calcium carbonate, may reduce the concentration of the calcium ions in the solution, at the time of precipitation, to a very low value, perhaps beneath that required for reducing the solubility of the calcium fluoride to the minimum. We have found that calcium fluoride can be precipitated and filtered practically quantitatively with ease, even in the absence of calcium carbonate or other co-precipitant, thus avoiding the subsequent troublesome and often incomplete removal of this from the precipitate. This ease of precipitation and filtration can be achieved by paying attention to the conditions under which the calcium fluoride is precipitated, and also to the method of filtering. The method which we advocate provides for an excess of calcium chloride for reducing the solubility of the calcium fluoride. For filtering off the precipitate we suggest the use of a paper-pulp filter* as absolutely essential, not only because this retains the precipitate of calcium fluoride more effectively than a folded filter paper, but also so that the washing process may be carried out with the minimum of washing liquid. It is probably from a lack of attention to these points that the calcium fluoride method has acquired a reputation for a tendency to give unsatisfactory results. The statement made in the recent textbook of Hillebrand and Lundell (*Applied Inorganic Analysis*, 1929), that ammonium chloride in the solution "holds up" the precipitate of calcium fluoride, has not been confirmed. We have obtained at least as good results from precipitation in presence of ammonium chloride as in its absence. Indeed, the presence of ammonium chloride is essential in applying the calcium fluoride method to solutions containing sulphate, *e.g.* nickel-plating solutions, because, by virtue of the greatly increased solubility of calcium sulphate in ammonium chloride solution, the precipitation of calcium sulphate may be substantially prevented.

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* Communication from the Research Department, Woolwich.

PRECIPITATION OF CALCIUM FLUORIDE IN ABSENCE OF SULPHATES.—Experimental work on the following lines was undertaken to find the best conditions for precipitating fluoride as calcium fluoride, and it is shown that the precipitation can be successfully carried out from solutions having a wide range of *p*H values, containing fluoride either alone or with nickel chloride, boric acid, and considerable quantities of ammonium chloride.

The Standard Fluoride.—Some difficulty was at first experienced in obtaining a pure fluoride on which to base the work. Commercial "pure" sodium fluoride is liable to contain, among other substances, sodium fluosilicate, the solubility of which is very near that of sodium fluoride; the salt is extremely difficult to recrystallise, because both the solubility and the solubility gradient with temperature are low; in any case, its satisfactory recrystallisation demands large platinum vessels. Potassium fluoride, being a hydrated salt and somewhat hygroscopic, was considered unsuitable. A possibility which had to be abandoned was that of using diluted "A.R." hydrofluoric acid standardised by titration; this acid, on analysis, was found to contain about 1 per cent. of silicon as hydrofluosilicic acid, which, since it behaves on titration with alkali in the cold as a dibasic acid, vitiates the calculation of the total fluorine as hydrogen fluoride. We adopted, as a standard material, sodium fluoride prepared as follows:

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* The preparation of these filters from "ashless" filter paper macerated with water is described in, *e.g.* the following books: Picard, *Steel Analysis*, 1914, p. 5; Hackney, *Quantitative Inorganic Analysis*, 1930, p. 15.

A fairly strong solution of potassium fluoride was prepared in a platinum dish and filtered through a gutta-percha funnel, the filtrate being allowed to drop slowly into a well-shaken, equimolecular, roughly half-saturated solution of sodium chloride contained in a pyrex flask. The finely crystalline sodium fluoride, which rapidly separated out, was filtered off without delay, washed with water, and dried at 100° C. Its weight remained unchanged at 500° C., showing that it was anhydrous. Tests showed that it was practically free from chlorides.

Precipitation of Calcium Fluoride from Neutral Solution.—Solutions having the volumes shown in Table I were made up to contain various amounts of sodium fluoride. These solutions were rendered slightly acid with hydrochloric acid; a few drops of methyl red indicator (0·02 per cent. in 50 per cent. alcohol) and 10 c.c. of calcium chloride solution (10 per cent. $CaCl_2$) were added, followed by dilute ammonia until the indicator just changed to yellow. The liquids were boiled for about one minute, cooled in running water for fifteen minutes, and filtered through small compressed pulp filters. The precipitates were washed four times with cold ammonium nitrate solution (5 per cent.) and twice with cold water; about 10 c.c. of liquid was used for each washing. The filters were heated in weighed platinum capsules at a moderate temperature (400 to 600° C.) until all the carbonaceous matter had burned off, and then at about 800° C. for 10 minutes. In some cases the residue of calcium fluoride was converted to calcium sulphate. The results are shown in Table I.

TABLE I

Fluorine added. Grm.	Volume of solution before precipitation. c.c.	Weight of residue (CaF_2). Grm.	Fluorine found. Grm.	Weight of residue ($CaSO_4$). Grm.	Equivalent to fluorine. Grm.
Nil–Blank	50	[0·0008]		[0·0018]	
0·0100	50	0·0216–0·0008	0·0101	0·0375–0·0018	0·0099
0·0200	50	0·0424–0·0008	0·0202	0·0744–0·0018	0·0202
0·0400	50	0·0837–0·0008	0·0404	0·1468–0·0018	0·0404
Nil–Blank	100	[0·0011]		[0·0023]	
0·0100	100	0·0201–0·0011	0·0092	0·0349–0·0023	0·0093
0·0200	100	0·0407–0·0011	0·0193	0·0712–0·0023	0·0192
0·0400	100	0·0815–0·0011	0·0391	0·1430–0·0023	0·0392

The high "blank" obtained in this series of experiments was most probably caused by carbon dioxide being present in the water and by ammonia being used and gaining access to the solution during the boiling, etc. By using a washing liquid containing 1 per cent. of acetic acid and 5 per cent. of ammonium nitrate, the "blank" was reduced to about 0·0003 grm., as shown in Table II. This washing liquid was adopted throughout the subsequent work.

TABLE II

Fluorine added. Grm.	Volume of solution before precipitation. c.c.	Weight of residue (CaF_2). Grm.	Fluorine found. Grm.	Weight of residue ($CaSO_4$). Grm.	Equivalent to fluorine. Grm.
Nil–Blank	50	[0·0003]		[0·0005]	
0·0100	50	0·0200–0·0003	0·0096	0·0344–0·0005	0·0095
0·0200	50	0·0408–0·0003	0·0197	0·0713–0·0005	0·0197
0·0400	50	0·0815–0·0003	0·0395	0·1431–0·0005	0·0398

Precipitation of Calcium Fluoride from Acid Solution.—Table III shows the results obtained in the precipitation of calcium fluoride from solutions containing various concentrations of acetic acid. The solutions (50 c.c.) containing sodium fluoride were made just alkaline to brom-phenol blue, and acetic acid was added to give the concentrations shown; the method of precipitation, etc. already outlined was followed.

TABLE III

Fluorine added. Grm.	Acetic acid. Per Cent.	Weight of residue (CaF_2). Grm.	Fluorine found. Grm.	Weight of residue ($CaSO_4$). Grm.	Equivalent to fluorine. Grm.
Nil–Blank	1	[0·0002]		[0·0003]	
0·0100	1	0·0198–0·0002	0·0095	0·0339–0·0003	0·0094
0·0200	1	0·0408–0·0002	0·0197	0·0711–0·0003	0·0197
0·0400	1	0·0810–0·0002	0·0394	0·1409–0·0003	0·0392
0·0100	10	0·0194–0·0002	0·0094		
0·0100	25	0·0198–0·0002	0·0095		
0·0398	10	0·0810–0·0002	0·0393		
0·0398	25	0·0810–0·0002	0·0393		
0·0398	50	0·0810–0·0002	0·0393		
Nil–Blank	25	[0·0002]			

Precipitation of Calcium Fluoride from Solutions containing Boric Acid, Nickel Chloride and Ammonium Chloride.—The results recorded in Table IV were obtained. In each experiment the fluoride was precipitated by the addition of 10 c.c. of calcium chloride solution (10 per cent. of $CaCl_2$), the fluoride solution containing 1 per cent. of acetic acid.

TABLE IV

Added.		Found.			
Fluorine. Grm.	Grm.	CaF_2. Grm.	Fluorine. Grm.	$CaSO_4$. Grm.	Equivalent to fluorine. Grm.
0·0200	0·02 H_3BO_3	0·0397	0·0193		
0·0200	0·20 ,,	0·0397	0·0193		
0·0200	0·5 NH_4Cl	0·0402	0·0196		
0·0200	5·0 ,,	0·0423	0·0206		
0·0200	0·20 H_3BO_3; $5NH_4Cl$	0·0406	0·0198	0·0700	0·0195
0·0400	0·02 H_3BO_3	0·0794	0·0387		
0·0400	0·20 ,,	0·0810	0·0394		
0·0400	0·20 H_3BO_3; $5NH_4Cl$	0·0821	0·0400	0·1429	0·0399
0·0400	2·0 $NiCl_2.6H_2O$	0·0822	0·0400	0·1422	0·0397
0·0400	2·0 $NiCl_2.6H_2O$; $5NH_4Cl$	0·0840	0·0409		
0·0400	2·0 $NiCl_2.6H_2O$	0·0825	0·0402		
0·0400	2·0 $NiCl_2.6H_2O$; $5NH_4Cl$	0·0827	0·0402		

In the last two experiments precipitation took place from 10 per cent. acetic acid solution instead of from 1 per cent. solution.

THE INTERFERENCE OF IRON AND ITS AVOIDANCE.—In planning a process for the determination of fluoride in nickel-plating solutions attention had to be given to the interference of (ferric) iron. In proportion to the amount of ferric salts present, the precipitation of calcium fluoride is either partly or completely prevented. Attempts to overcome this interference by the addition of organic hydroxy-compounds, *e.g.* mannitol, lactic acid, citric acid, etc., were unsuccessful. It was found, however, that quantitative precipitation of the fluoride could be effected if the iron in the solution was reduced to the ferrous condition, the following method being adopted:—To the solution containing 10 per cent. of acetic acid, were added 10 c.c. of calcium chloride solution (10 per cent.) and 1 c.c. of hydrazine hydrochloride solution (20 per cent.). The solution was heated to boiling. The brown colour of the ferric acetate (which is not precipitated) rapidly became bleached, and the calcium fluoride then precipitated. After boiling for about half a minute, the solution was cooled in running water for 15 minutes, and the filtration, etc., of the calcium fluoride carried out as usual. Table V contains the results obtained.

TABLE V.

Added.					Found.	
Fluorine. Grm.	Iron (as $FeCl_3$). Grm.	Nickel (as $NiCl_2$). Grm.	Boric acid. Grm.	Ammonium chloride. Grm.	Calcium fluoride. Grm.	Fluorine. Grm.
0·0400	0·10	—	—	5·0	0·0811	0·0395
0·0400	0·05	0·5	0·20	5·0	0·0811	0·0395
0·0400	0·05	0·5	0·20	5·0	0·0821	0·0400

When the amount of iron is small, it can be removed from the solution by precipitation as ferric hydroxide, without causing any loss of fluoride. This method would appear to be more convenient than the above in the determination of fluoride in nickel-plating solutions, and will be referred to later in that connection.

PRECIPITATION OF CALCIUM FLUORIDE FROM SOLUTIONS CONTAINING SULPHATE.—The low solubility of calcium sulphate in water renders it practically impossible to precipitate calcium fluoride quantitatively in a pure condition by the addition of calcium chloride to a solution containing fluoride and sulphate. This is especially true of a nickel-plating solution, because the ratio of sulphate to fluoride is large. We have found, also, that there is a noticeable tendency for calcium sulphate to be adsorbed by a precipitate of calcium fluoride when this is formed in a solution only partly saturated with calcium sulphate. We have, however, been able to take advantage of the enhanced solubility of calcium sulphate in ammonium chloride solution to work out a feasible process for precipitating calcium fluoride from a solution containing much sulphate. By employing a regulated excess of calcium chloride, only a small quantity of calcium sulphate is precipitated with the calcium fluoride; a correction can be made for this by deducting from the weight of the precipitate the weight of the calcium sulphate, calculated from a determination of sulphate in it. The best results were obtained by precipitating the calcium fluoride from a neutral or slightly ammoniacal solution; good results, in the presence of sulphate, were not obtained when solutions containing acetic acid were used. Details of the method adopted are incorporated in the following process proposed for the determination of fluoride in nickel-plating solutions.

DETERMINATION OF FLUORIDE IN FLUORIDE-BORATE NICKEL-PLATING SOLUTIONS.—Ten c.c. of the solution are diluted to 25 c.c., and 5 c.c. of ammonia* (sp. gr. 0·88) are added. The liquid is boiled for about half a minute and filtered through a small filter paper (*e.g.* Whatman, 7 cm., No. 41). The beaker is rinsed out four times with 5 c.c. of 5 per cent. ammonia on to the filter, which is allowed thoroughly to drain each time. The precipitate, if any, of ferric hydroxide is rejected, and the filtrate, having a volume of about 45 c.c., is made slightly acid with concentrated hydrochloric acid, and 2·5 c.c. of calcium chloride solution (10 per cent., made from anhydrous salt) are added slowly, drop by drop (this quantity suffices for the amount of fluoride normally to be found in these nickel-plating solutions, *i.e.* up to about 10 grms. of sodium fluoride per litre; see note below); the solution is then made just alkaline with ammonia, boiled for about half a minute, and cooled in running water for fifteen minutes. The precipitate of calcium fluoride (with adsorbed calcium sulphate) is filtered off on a small well-compressed pulp filter and washed four times with 5 per cent. ammonium nitrate solution containing 1 per cent. of acetic acid, and then twice with cold water. The total amount of washing liquid used should not exceed 50 c.c. The filter, with the precipitate, is transferred to a platinum capsule, heated at about 400–500° C. until the carbonaceous matter has been destroyed, and then ignited at 700–800° C. for ten minutes. After weighing, 5 c.c. of concentrated hydrochloric acid (free from sulphate) are added to the residue in the dish, which is then heated until all the acid has evaporated. This treatment is repeated until the residue has been completely attacked and a clear solution can be obtained in the 5 c.c. of acid. The 5 c.c. of solution are transferred to a conical flask, diluted to about 100 c.c., and heated to boiling, and 20 c.c. of barium chloride (10 per cent.) solution are added slowly. The barium sulphate is allowed to settle, and is then filtered off, washed, ignited, and weighed. The equivalent weight of calcium sulphate is deducted from the weight of the original precipitate, and the weight of calcium fluoride is thus obtained.

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* This will provide the necessary amount of ammonium chloride.

TABLE VI

	Added.					Found.					
No.	Fluorine. Grm.	Nickel sulphate. Grm.	Boric acid. Grm.	Iron, as ferric sulphate. Grm.	Calcium chloride (10 per cent. solution). c.c.	Impure Calcium fluoride. Grm.	Barium sulphate. Grm.	Calcium sulphate. (calc.) Grm.	Nett Calcium fluoride. Grm.	Fluorine. Grm.	Fluorine (corrected). Grm.
1	0·0100	2·4	0·2	0·01	2·5	0·0195	0·0045	0·0026	0·0167	0·0081	0·0101
2	0·0200	2·4	0·2	0·01	2·5	0·0419	0·0080	0·0046	0·0373	0·0182	0·0202
3	0·0400	2·4	0·2	0·01	2·5	0·0891	0·0175	0·0101	0·0790	0·0385	0·0405
4	0·0800	2·4	0·2	0·01	3·5	0·1750	0·0300	0·0174	0·1576	0·0768	0·0788
5	*0·0216	2·4	0·2	—	2·5	0·0454	0·0095	0·0055	0·0399	0·0194	0·0214
6	*0·0288	2·4	0·2	—	2·5	0·0622	0·0138	0·0080	0·0542	0·0264	0·0284
7	*0·0592	2·4	0·2	—	2·5	0·1298	0·0300	0·0174	0·1124	0·0547	0·0567†

* Amount of fluoride added to test solutions unknown to the analyst.

† Low result indicates that insufficiency of calcium chloride was added.

Table VI shows results which were obtained with solutions made up to simulate nickel-plating solutions containing 240 grms. of nickel sulphate and 20 grms. of boric acid per litre, with different amounts of sodium fluoride added; to some of the solutions iron was added, in greater amount, however, than would be expected in a nickel-plating solution, in order to verify its non-interference in the process. It will be noticed that the results are lower than the theoretical by a fairly constant amount, *viz.* 0·002 grm.; this seems due to a solubility effect, probably introduced by the high nickel and sulphate concentration of the solution, and it is, therefore, suggested that a correction of this order should be applied to the results obtained.

The addition of 2·5 c.c. of calcium chloride solution (10 per cent.) is satisfactory for the precipitation (in a volume of 50 c.c.) of fluorine from 10 c.c. of nickel-plating solution containing not more than 10 grms. of sodium fluoride per litre, which is a concentration not usually exceeded in practice. In the event of the solution containing a higher concentration of sodium fluoride, it would be necessary to increase the amount of calcium chloride for the precipitation; in Experiment 4 (in the table), in which 0·08 grm. of fluorine was present in 10 c.c. (corresponding with 17·7 grms. of sodium fluoride per litre), 3·5 c.c. of calcium chloride were used. It is recommended, however, that this process should be carried out as described, and if the result comes out at more than 10 grms. of sodium fluoride per litre, the determination should be repeated, using slightly more calcium chloride for the precipitation. The amount of calcium chloride for the precipitation must be controlled with reasonable care, to keep the correction for calcium sulphate in the final precipitate as low as possible, yet (at the same time) to give a sufficient excess of calcium ions in the solution for the fluoride precipitation.

Scientific Documentary Evidence in Criminal Trials

By C. AINSWORTH MITCHELL, D.Sc., F.I.C.

(Read at the Summer Meeting, North of England Section, July 4, 1931)

When your Honorary Secretary (Mr. J. Stubbs) asked me to read a paper at your Summer Meeting, and this request was repeated by our President, I felt that it would be ungracious not to respond, and I, therefore, agreed to give a survey of the scientific evidence which may be based on documents in criminal trials and to illustrate this by cases within my own experience.

Scientific documentary evidence is, of course, circumstantial in character, and it is a common practice for counsel for the defence in criminal trials to decry all circumstantial evidence, notwithstanding the fact that it is often more trustworthy than personal testimony. Apart from that, if it were excluded, there would be few convictions even of dishonest tradesmen, and fewer still of the inveterate poisoner, who is the last person to advertise his intentions or to let his acts be seen.

The rules that govern documentary evidence are the same as those governing any other expert evidence. For example, since the leading case of *Seaman* v. *Netherclift* (1876), a witness on oath is in a privileged position, whether he asserts that a sample has been grossly adulterated, or that a signature is a forgery. There are also certain judicial decisions which have been given in connection with documents, and are also applicable to scientific evidence in general. For instance, Mr. Justice Finlay, in the case of *Rex* v. *Henry* (1929), allowed a tracing to be shown to the jury, and in the case of *Rex* v. *Podmore* (1930) the Lord Chief Justice held that a photograph upon which marks had been made with the object of directing the attention of the jury to certain details in the original document, was admissible, since it went to strengthen the evidence.

Many of the scientific data upon which evidence as applied to documents can be based have been accumulated comparatively recently, and new cases frequently present problems for which no solution can be found in textbooks. These may best be considered under the headings of the various materials, beginning with ink.

EVIDENCE RELATING TO INKS.—*Differentiation of Writing Inks.*—The first occasion on which evidence as to differences in ordinary blue-black writing inks on a document was given in this country was at the trial of Brinkley in 1907 (*Rex* v. *Brinkley*). In that case a forged will was the motive for an unintentional murder (if that is not a contradiction in terms), for the prisoner had tried to poison a man whose name appeared as a witness on the will, but who had stated that he had signed only what he had been told was a petition for an outing. A bottle of stout, dosed with prussic acid, was left in this man's lodgings, where it was drunk by his landlord and landlady, both of whom died. An important point in the evidence was whether the statement about the signing of a petition for an outing in a public-house was true, and accordingly the ink used in that public-house was compared with the ink in the signature upon the will. Chemical tests could not be made, since the President of the Probate Court refused his permission for the will to be touched, but, fortunately, an optical examination was sufficient for the purpose. The ink ("Azuryte") from the public-house contained a particularly brilliant blue dye, which enabled it to be distinguished readily from most other inks in common use at that time; and by first matching the inks on the will under the microscope, and then preparing broad colour bands which could be compared by means of a tintometer, it was possible to demonstrate in Court that the ink from the public-house agreed exactly with the ink in the signature on the alleged will, and also that there were three separate inks upon that document. Brinkley admitted this, but tried to explain it away by saying that he had given two bottles of ink to a little girl. He was convicted and executed.

Prior to the war, English ink manufacturers were using a large variety of blue dyes as provisional colouring matters, and this was helpful for distinguishing between different inks, whether by optical or chemical methods (see ANALYST, 1908, **33**, 80), but for some years past the Board of Trade has consistently refused to allow any dyestuffs to be imported for ink-making, with the result that the provisional colouring matter in writing ink is usually the same "Ink Blue" (Soluble Blue), and chemical tests must now be based, in the main, on the different proportions of dye, tannin substances and iron in the inks.

Osborn's comparison microscope, which has been devised since the Brinkley case, is a valuable instrument for comparing colours and recording their Lovibond values, although it is not advisable to attempt to demonstrate its use to a jury; the colour-strip method, as used in that trial, is still the simplest way of showing in Court differences of colour in inks on a document.

Gradation of Colour.—The colour of an ink will naturally vary with such conditions as the length of time the ink has remained exposed to the air in an inkpot, or the time it was left upon paper before blotting. These points are of considerable importance in judging whether the whole of a given piece of writing was done at the same time, as may readily be seen on comparing successive entries in hotel registers. It was a significant fact that in the case of *Bishop of Lincoln* v. *Wakeford* (1921) the disputed words "and wife" in the two entries in the hotel book agreed exactly in gradation of tone with the preceding words, "J. Wakeford." It would have been an exceptionally skilful forger who could have twice completed those entries in ink of exactly the correct shade.

Photographic Differentiation.—Another optical method of distinguishing between two writing inks, one of which is richer in blue units than the other, is by means of photography on an ordinary "process" plate. When such difference in colour is present, two inks which, when examined under the microscope, appear to match one another, may show a pronounced difference when photographed, the ink richer in red appearing much darker in the print than in the original document. This method afforded conclusive evidence in the case of *Rex* v. *Cornwallis* (1919), in which a woman produced a letter acknowledging the receipt of £200, with a final "0" added to the amount in a different ink.

A remarkable case in which a photographic reproduction suggested forgery was that of *Hawes* v. *Skelton* (1924), in which a will was discovered in the pocket of the overall of a woman who was bathing a dog. The signature on this will showed different colours, and had manifestly been re-touched, but the Judge (Mr. Justice Horridge) was not satisfied that these abnormalities were sufficient to condemn the document, and deferred the case for a scientific opinion. The bottle of ink with which the document was alleged to have been signed was produced in Court. It was said to contain a mixture of three different inks bought at a sale, and experiments showed that this mixture was capable of accounting for all the abnormalities found on the document. It produced writing of different colours according to the depth to which the pen was dipped into the ink, and the ink ran badly from the nib, necessitating re-touching of the writing. As a result of this evidence the Judge pronounced in favour of the will.

Age of Ink in Writing.—The change of colour which rapidly takes place when ink begins to oxidise on paper may sometimes afford proof that writing is recent. Thus, in a claim brought against an insurance company by a clothier for the alleged loss of his stock by fire, it was found that entries in a stock book, which purported to be two years old, darkened perceptibly in the course of three or four days, and must, therefore, have been comparatively recent. The colour readings in tintometer units were taken on successive days during the period of the test, and were checked by another observer, so that there was no doubt as to the progressive change in colour. But, at best, evidence of this kind is unsatisfactory, since it is subjective in character, and cannot be supported by photographic proof or checked by subsequent examination.

Chemical evidence of the age of ink is much more convincing than colour records, since the test can be repeatedly checked, as I have shown in my discussion on the subject (Analyst, 1920, **40**, 247). In the case of *Rex* v. *Pilcher* (1911) special permission was obtained from the President of the Probate Court for chemical tests to be applied to the inks upon a will purporting to be thirteen years old. All the inks on the document readily ran over the paper when treated with reagents, and formed blue smudges, whereas the inks on the older counterfoils of cheque books of the deceased woman, which dated back for six or eight years, remained practically unaffected by the reagents under the same conditions; hence the inks on the disputed will could not have been as old as its date. After this evidence had been given, Colonel Pilcher confessed that he had uttered the will, knowing it to be a forgery, and he was sentenced to three years' imprisonment.

ANACHRONISMS IN INKS.—On several occasions fraudulent claims for old-age pensions have been exposed owing to the fact that the entries in family Bibles, produced as evidence of age, were written in blue-black ink containing an aniline dye, whereas aniline dyes had not been discovered at the dates mentioned. Such dyes appear to have been introduced into writing fluids in this country about 1880, but the earliest instance I have yet found in old ledgers was an entry written in 1885.

A more uncommon anachronism was disclosed in connection with two documents in the case of *Rex* v. *Rogers* (1930). It would need the pen of a Thomas Hardy to do justice to the story unfolded at that trial of a man who had foisted forged documents on to an ignorant old woman, an old-age pensioner, and had received £5 from her. She was a descendant of William Penn, the Quaker, and claimed to be entitled to his estates. The two documents, which she was led to believe would establish her claim, were genuine old parchments, one of which related to a conveyance of land by the Earl and Countess of Yarmouth in 1688. In each instance the name of "William Penn" appeared after the signatures of the other witnesses, and was apparently in the same kind of iron-gall ink which had disintegrated with age, leaving a residue of oxidised iron compounds. But the inks of the William Penn signatures, unlike all other writing on the documents, contained no iron, and when treated with a minute drop of hydrochloric acid, became milky. This was found to be due to silver, which had become brown —in other words, the ink had the characteristics of a silver marking ink. This discovery became still more significant when counsel for the defence asked whether the forgery could have been perpetrated by William Ireland, who was responsible for the wholesale forgery of Shakespearian documents at the close of the eighteenth century. Ireland afterwards wrote a full confession of his methods, and, from the description of his ink, he was evidently using a preparation containing a silver salt.*

The answers to the question raised about Ireland were: (1) Ireland did not use a steel pen for his forgeries, as had manifestly been used in the Penn forgeries

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* *The Confessions of William Henry Ireland, containing the Particulars of his Fabrication of the Shakspeare Manuscripts* (1805), p. 39. "One of the journeymen, looking at the manuscript, informed me that he could give me a mixture that would resemble old ink much more than that which I had used; and, in consequence of my request, he immediately mixed together in a phial three different liquids used by bookbinders in marbling the covers of their calf bindings. These ingredients, being shaken up, produced a fermentation; when, the froth having subsided, the liquid was of a dark brown colour. The young man then wrote his name with this mixture, but it was very faint on the paper; however, on holding it for a few seconds before the fire, the ink gradually assumed a very dark brown appearance. . . . It was with the same ink I afterwards wrote the Shaksperian manuscripts. Their scorched appearance originated in my being compelled to hold them to the fire, as before stated; and, as I was constantly fearful of interruption, I sometimes placed them so near the bars as to injure the paper; which was done in order to complete and conceal them as speedily as possible from any unexpected person who might come suddenly into the chambers." (*Cf.* Plate, Fig. 4.)

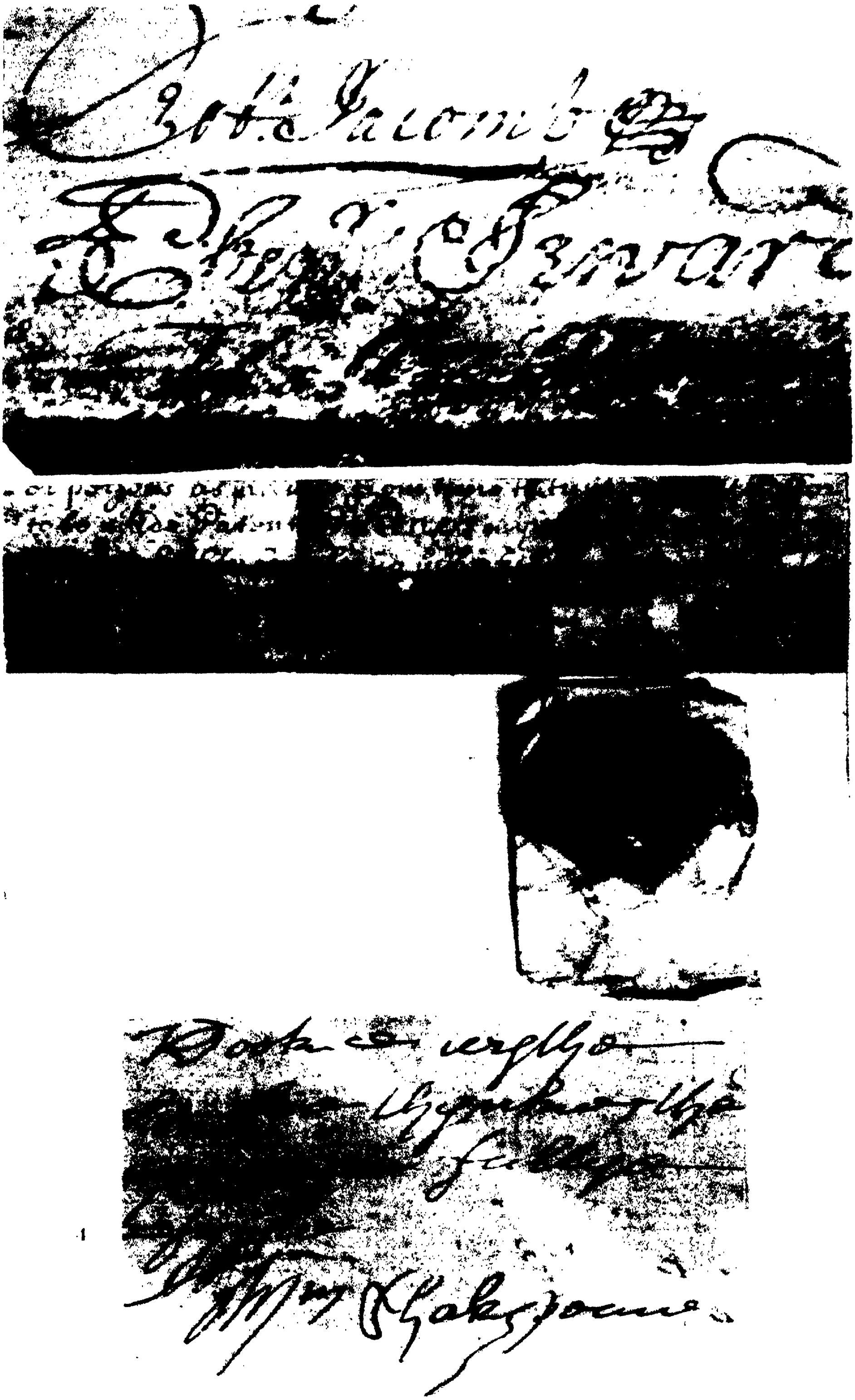
(Fig. 1); steel pens were not invented until 1808. (2) Ireland confined his attentions to fifteenth and sixteenth century documents; in those days there would have been no motive for producing autographs of William Penn. (3) There were no characteristics in the writing to suggest that Ireland had had anything to do with the forgery, which was a clumsy imitation of the genuine writing, as may be seen by comparison with the signature on one of the genuine Penn documents brought into Court for comparison (see Plate, Figs. 2 and 3).

The prisoner was found guilty of uttering the forged documents, and was sentenced to a term of imprisonment.

Fig. 1. Enlargement of forged signature of William Penn—showing the effect of a steel nib.

Ink in Creases in Paper.—The way in which a paper has been folded may be significant, especially when there is writing across the fold. If the writing has been added since the folding of the paper, it will sometimes be found that the ink has spread slightly along the crease, owing to the paper having become more porous through a break in the surface sizing after repeated folding in the same place. In a case tried in 1929, a fact of this kind afforded proof that some writing on an agreement was not so old as the document itself.

Sequence of Strokes in Writing.—The conditions under which it is possible to be certain that a stroke in writing which appears to be on the top of another stroke really is uppermost have been discussed in a previous paper (Mitchell and Ward, Analyst, 1927, 52, 580). Briefly, the rule is that if one of the pigments in the intersecting lines is a thin film of colour, as in stamping ink or blue-black writing ink which has been blotted immediately after writing, it is not possible to express an opinion which line was made first; but, if the pigment is sufficiently dense, as in printing ink, or if a layer of solid pigment forms, as when iron-gall inks oxidise on paper, definite conclusions may be drawn. These conditions were present in the case of *Rex* v. *Cohen*, discussed in a former paper (Analyst, 1920, 45, 252). In another case (*Lonnen* v. *Lonnen*) a codicil to a will, which two witnesses swore that they had seen signed, was upset by the fact that at two points the writing of the codicil intersected the writing of the signature of the testator,



Robt Iacomb

Wm Shakspeare

and could be demonstrated by means of enlarged photography to be uppermost, thereby proving that the codicil had been inserted after the will had been signed.

With black lead pencil writing the sequence of strokes can always be determined by the lines of the silver striations (due to the impurities in the graphite or to the added clay), which are seen when the strokes are examined in oblique lighting (see ANALYST, 1922, 47, 379).

DIFFERENTIATION OF PENCIL PIGMENTS.—In some cases microscopical differentiation of pencil marks is possible (*J. Soc. Chem. Ind.*, 1919, 38, 381T), but great caution is necessary, since it is possible, by wetting the lead or varying the pressure, to alter the way in which pigment is deposited on the paper, and the series of strokes containing approximately the same amounts of pigment must be chosen for the comparison. The differentiation of old graphite pencils from modern composite pencils is usually practicable, however, owing to the fact that the silver striations of the former are irregular and interrupted, whilst those of the latter are like strings of beads.

Chemical tests depend upon the fact that graphites contain widely differing amounts of iron and chlorides, and, in exceptional cases, there is sufficient titanium to respond to a micro-chemical test. Coloured pencils can usually be distinguished from one another without much difficulty (see ANALYST, 1922, 47, 385).

COPYING INK PENCILS.—An outline of the methods of distinguishing between the pigments of copying ink pencils on paper will be found in THE ANALYST (1917, 42, 3). There is more scope than with ordinary blacklead pencils, owing to the fact that there are usually three constituents present—kaolin clay, violet dyestuff, and blacklead, and that the proportions of these affect the reactions given by the writing. In the case of *Rex* v. *Wood* (1907), in which charred fragments of paper were found in the grate of the house where a woman had been murdered, it was possible to prove by a series of tests that the pigment on the paper agreed with that of a copying ink pencil in the possession of an artist who was accused of the murder. Ultimately he admitted having written the letter, but was acquitted of the murder.

The possibility of such pigments resisting the action of sea-water for some weeks was raised in the case of *Macbeth* v. *King* (1916), in which the genuineness of a stave of wood with a message supposed to have originated from a steamship, presumably sunk by a torpedo, was a point at issue. Experiments described to the Court showed that copying ink pencil writing on a piece of oak would not be obliterated by six weeks' exposure to sea-water and air.

The behaviour of copying ink pencil writing towards various solvents had to be determined in the case of *Rex* v. *Podmore* (1930), in which a scrap of paper, about two inches square, which was found behind a barrel in a garage at Southampton where a man had been murdered, led ultimately to the conviction of the murderer. This fragment was caked with dirt and soaked in oil, and had been repeatedly trodden under foot, and the problem was to remove the dirt and oil, without also removing the pigment of the copying ink pencil. After numerous experiments with various makes of copying ink pencil, petroleum spirit was found to be suitable for the purpose, and a message from a man calling himself "W. F. Thomas" was left upon the paper. Until then, it was not known that anyone of the name of "Thomas" (an alias of Podmore) had been in any way connected with the victim.

The use of ultra-violet light made it possible to read much more of this message than could be brought out by an ordinary photograph, but, to avoid any suggestion of the use of the imagination, the evidence on this fragment at the trial was restricted to the words and characters which the jury could see for themselves.

INDENTATIONS IN PAPER.—Another document produced at this trial was a leaf from a note-book showing indentations which had, presumably, been made by the pressure of a pencil on another leaf of the book subsequently torn out. By means of photography with the use of oblique lighting to illuminate the edges of the indentations, words relating to bogus orders, with the initials of "Thomas," were rendered visible, and this formed a further link in the evidence which led to the conviction of Podmore.

SECRET WRITING.—The search for secret writing in a document is usually only needed on special occasions, such as the detection of espionage in war time or irregular communication with the outside world by prisoners. The substances which are capable of being used as invisible inks are almost innumerable, but, broadly speaking, they fall into two classes—those forming a coloured compound on treatment with a mordant, and those which become visible when examined by special optical methods such as ultra-violet light. A discussion of the subject will be found in my book, *The Scientific Examination of Documents*, p. 153 (Chas. Griffin & Co.), and in Lucas's *Forensic Chemistry*, 2nd Ed., p. 105 (E. Arnold & Co.).

In the earlier trials of German spies during the war (*Rex* v. *Kuepferle* (*Times* Report, May 15, 1915), *Rex* v. *Müller and Hahn*, and some others), the primitive method of writing with lemon juice was employed, and evidence was required to prove that steel pens in the possession of the accused had deposits upon them consistent with their having been dipped into lemon juice, whilst cut lemons gave reactions for iron at points where, apparently, something had been inserted into them. In later trials, more elaborate methods of secret writing were employed, as may be gathered from the story of these spy cases in Felstead's *German Spies at Bay* (Hutchinson).

The knowledge of the use of saliva for secret writing, and of its development with a dilute solution of ink, was common property long before the war (*cf.* Dennstedt and Voigtländer, *Lehrbuch der gerichtlichen Chemie*, 1907, p. 122). In a study of the action of saliva upon iron-gall ink (ANALYST, 1920, **45**, 256) I have shown that it behaves like an oxydase, accelerating the oxidation of the ferrous tannate and forming a compound which is distinct from that which forms normally when ink is oxidised by exposure to the air. The process of the development with ink of writing done with saliva thus appears to be partly physical (absorption of dye where the fibre of the paper has been indented) and partly chemical (accelerated oxidation of the ink).

TYPEWRITING.—Fortunately it is not generally realised, especially by those who are given to writing anonymous letters, that typewriting can be identified with that produced by a particular machine, with a much greater degree of certainty than the identification of handwriting. Apart from the fact that each manufacturer uses a different fount of type, which is usually varied in successive models, every machine has its individual faults of alignment and displaced and imperfect letters, by means of which its identity, and, in certain cases, its age, can be established.

The best methods and instruments for recognising and demonstrating such identity are described by Osborn in his *Questioned Documents* (2nd Ed., p. 437, *et seq.*). Identity in the relative positions of various letters is shown by means of photographs taken under glasses ruled in standard squares, and the typing produced by battered letters is easily recognised, even by an unintelligent jury, when shown in an enlarged photograph. Osborn cites many examples of cases in which the evidence derived from a study of typewritten documents has been incontrovertible, and these might be supplemented by numerous cases in this country. Among the most recent of these is *Rex* v. *Parry* (1930), in which a former tax collector was convicted of inducing an old man and his wife to make a successful fraudulent claim for the repayment of income tax, by which he also benefited. He denied that the fraudulent returns had originated from his office, but the typing upon them agreed in all its characteristics with that upon admitted letters typed on his machine, and this was one of the facts which led to his conviction.

PRINTED MATTER.—Much of what has been said about the differentiation of typing applies also to printed characters. The founts used by different printers have distinctive differences, and parts of certain letters tend to become defective with use. Evidence on such points is required when the authenticity of a printed document, such as a passport (*vide* infra), is questioned.

SEALS.—The methods of forging seals have been fully described by Türkel in his *Fälschungen*, p. 14 (*cf.* ANALYST, 1931, 56, 141). Photographic methods can be used for detecting such forgeries, and in some cases chemical evidence may be decisive. For example, in the case of *Rex* v. *Fink* (1911), the defence set up in a case in which a cheque had been forged was that the forgery had been committed after the cheque had been posted in a sealed envelope. Chemical tests, however, were applied to the wax of Major Fink and to the seal on the letter, and gave practically identical results for colouring matter, ash and sulphate, whereas the corresponding figures given by the wax from the post office where the letter was posted, and by six samples of red sealing wax, bought at random, were totally different.

STAMPS AND POSTMARKS.—As an illustration of the kind of information that may be gathered by minute examination of the stamp and postmark on an envelope, reference may be made to a case in which an anonymous letter, bearing a German postmark and registration mark, was received in a London office. Microscopical examination showed that only that part of the postmark upon the stamp was genuine, the remainder of the circle upon the paper having been crudely completed. Ultimately it was found that the letter had originated from within the office, and that the stamp and registration number had been detached from a genuine registered German letter (the receipt for which had been duly signed), and then put on to another envelope containing the anonymous letter, after which the missing part of the postmark had been replaced by hand, probably in Indian ink.

COMPOSITION OF THE PAPER.—The composition of the paper of a document may give useful suggestions, as in a case in 1914, in which the crudely forged notes of an Oriental bank were found to consist of pure flax. This suggested that the forgeries had probably emanated from Russia, as was subsequently found to be the case. Chemical tests, including the difference in the liberation (by the sizing) of iodine from potassium iodide and the determination of the acidity, afforded proof that the forged American passport produced by the German spy, Brekoff (*alias* Rowland), was not genuine, and evidence to that effect was given at his trial in 1915. In addition to chemical differences in the papers, the dyestuffs in the paper seals attached to the two documents were chemically different, and there were differences in the type in which the passports were printed. Among the printing defects was one which could easily be seen by the jury, for in the German version the American eagle had been docked of one of its tail feathers. There were also two other cases in which similar evidence was required.

ARTIFICIAL WATERMARKS.—The usual method of fabricating a watermark is to stamp the paper with the required device in a wax medium. Such spurious watermarks can, as a rule, be removed by treating the paper with a suitable solvent, as was found to be possible with certain notes which were being widely circulated. The fraud can also generally be made manifest by examining the document in ultra-violet light, when the artificial watermark will often show a pronounced fluorescence.

CHARRED DOCUMENTS.—I have discussed the methods of deciphering charred documents in previous papers (*Discovery*, 1924, **5**, 336; ANALYST, 1925, **50**, 174). Photographic methods, in which the charred fragment leaves an imprint of printed matter on a sensitised plate, depend upon the fact that printing ink which has been burned produces certain products which reduce silver salts, whereas charred cellulose has no action. In the communications mentioned above it was shown that different printing inks behave differently in this respect.

The other method of deciphering charred fragments is to continue the calcination further, for which purpose I have found the use of two pieces of wire gauze held in crucible tongs to be the most suitable, since the calcination can be controlled so that a coherent ash of the required colour is left. The lampblack of printing inks being less combustible than the char of paper, is left in its original black characters on white ash, whilst the alumina forming the bases of coloured printing inks remains in white on dark gray or blackish ash. Ordinary writing ink leaves a brownish residue of iron oxide, and the graphite of blacklead pencils and of copying ink pencils can be obtained as a residue on either white or grey ash.

The reason why so little writing was visible in the charred fragments in the Wood case (*supra*) was that the pigment of the copying ink (Swan) pencil which had been used contained no graphite.

This calcination method was found effective in a case in 1923, in which it afforded confirmation of the statement of a prisoner that he had accidentally burnt a bundle of bank notes of high value (*cf.* ANALYST, 1925, **50**, 178). Experiments made at that time showed that banknote paper contains so little filling material that it would be quite possible for a bundle of notes to be burnt and to leave very little coherent ash.

EVIDENCE ON HANDWRITING.—In the Podmore case, as in many other cases, questions of the identification of handwriting were raised. Sooner or later every chemist who undertakes the scientific examination of documents will be faced with the difficulty that his work must be incomplete unless it also deals with the examination of the writing on the documents; in fact, the Government Analysts of several of the Dominions and Colonies have been compelled by circumstances to take the subject of handwriting into consideration. In the interests of justice this is a move in the right direction, for much of the obloquy attaching to handwriting experts has been due to the fact that the earlier experts were frequently trained observers of minute detail (some were engravers), but they had not had a scientific training, and thus were prone to draw deductions which were not warranted by the observed facts. For instance, it was not uncommon for a handwriting expert to swear positively in the box that a given piece of writing was written by a particular person, whereas all that his observations justified was the inference that the characteristics of the writing agreed in form or writing habit with those of that person. Hence, when (as sometimes happened) it was found that more than one person shared those characteristics, a mistake had to be admitted, and discredit was brought upon the whole system of comparing handwriting.

Essentially, the judgment of handwriting is an analytical process, and depends upon the same fundamental rules of inductive logic (isolate, vary, measure) as are used in chemical analysis, but it is only exceptionally that a categorical conclusion can be drawn. The real value of the evidence is that it assists the Court to decide in which direction the balance of probability lies. For example, in the Podmore case the demonstrable facts were that the characteristics of the writing on the dirty fragment of paper and of the indented writing in the order book agreed with those of admitted writing of the accused. If it was not his writing, either it must have been a deliberate imitation of it, or there must have been two persons writing in exactly the same way and having the same initials, in the garage at Southampton at about the same time. It was for the jury to decide to what extent such a coincidence would be probable.

Or, again, in the case of Archdeacon Wakeford, the writing in the hotel register of the disputed words "and wife" agreed in all respects with admitted writing, even including the formation of a straight stroke as a sign for "and"—a habit which, until it was discovered in a volume of his manuscript, was unknown to those best acquainted with him. The only possible conclusion, other than that the writing was that of the accused, was that it was the work of an abnormally skilful forger, and it was then for the Court to decide whether such a forger could have been present at the hotel on two unexpected occasions, and could have added the words in such a way as to give the correct colour tones of the inks, as well as to reproduce the exact formation and style of the genuine writing.

TRACED FORGERIES.—Exceptionally, it is possible to state a conclusion in more positive terms than has been indicated, as, for example, in the case of *Beckerkunst* v. *Cohen* (1929), in which a forged will was produced, signed in an abnormal way by a woman whose condition was proved by medical evidence to be such that firm writing such as that of the signature in the document would have been impossible. In this case the results of comparison of the signature on the will with other signatures of the deceased woman supplemented the medical evidence, but there are instances when the evidence of documents by themselves may be conclusive. For example, in the case of *Rex* v. *Henry* (1929) a will was produced in terms which were practically identical with those on a draft of the will produced some months previously and then photographed. The formation of the words and their coincidence in position on the paper were explicable only on the assumption that one was, in part, a tracing from the other. When, subsequently, the production of the draft was again required, a third document, purporting to be this draft, was produced. This differed materially from the original draft, which had been photographed, and the space left where a piece had been cut from the edge of the former differed in size and shape from the corresponding space cut out in the latter; this space might have become larger in the interval between the times when the production of the draft will was demanded, but it was an impossibility for it to have shrunk.

On rare occasions the model which has served for a tracing may be discovered, and when it is, it may convert probability into certainty.* The classic instance of this type of forgery is the American case of Rice-Patrick, in which the signatures on four pages of a will agreed so closely with one another, that it was obvious that they must have been tracings, since no one would reproduce all the lines of the words in practically the same relative positions (see Osborn, *Questioned Documents*, p. 293).

When considering indications of tracing, there is one possibility which must not be overlooked. Solicitors sometimes indicate, by pencilling in a name, the place on a document where the signature is required, and sometimes a client whose intelligence is not of a high order will attempt to copy the pattern. In the case of *Oliver* v. *Oliver* (1930) there were features in a signature which, had they been in a letter and not upon a legal document, would have been conclusive that the signature was not genuine. The lines were wavering and hesitating, there were frequent breaks in unusual places, the formation of the letters was abnormal, and there were traces of graphite at the edges of some of the strokes. The significance of these points, however, was discounted by the fact that none of them was inconsistent with the other hypothesis, namely, that they were the results of an attempt to make a slavish copy of a signature previously outlined by a solicitor in blacklead pencil.

DISCUSSION

Mr. A. LUCAS confirmed Dr. Mitchell's statement that chemists who attempted to confine their work to the microscopical and chemical examination of documents were eventually compelled to take up the examination of handwriting. He gave a few examples of cases in his own experience, illustrating points which had been raised in the paper. In one of the cases cited, an ink that was alleged to be a mixed ink was proved not to be a mixture. In another case an anachronism was discovered in the composition of paper, which contained wood cellulose, although the date upon the document was about 60 years before that material was used as an ingredient of paper. Mr. Lucas also confirmed the value of Osborn's comparison microscope for the examination of documents.

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* In the case of *Rex* v. *Brown* (1931), which was *sub judice* when this point was mentioned, a signature showing indisputable indications of marks made with a dry point was found, and the coincidence of this signature with one on the document in dispute was conclusive evidence that the latter was not genuine.

The Biological Method for the Detection of Arsenic

BY A. F. LERRIGO, B.Sc., F.I.C.

IN view of the recent case of poisoning through arsenical wall-plaster (see p. 163), the following survey of the literature of the arsenic-liberating moulds may prove of interest; I made it some years ago in an attempt (abortive, as it proved) to investigate certain possibilities of the phenomenon.

1. "The capacity of the metalloid arsenic for combining with hydrocarbon radicles . . . has not been manifested . . . either in the mineral kingdom or as a result of the vital activities of living organisms. The special conditions under which this attraction becomes effective have been, without exception, established by the art of the chemist. All the organic arsenicals are synthetic products" (*Organic Compounds of Arsenic and Antimony*, by G. T. Morgan, 1918). The writer then states, in a footnote, that: "A possible exception to this generalisation is noted on p. 45 in reference to the production of di-ethyl arsine by the growth of moulds on carpets and wall-paper containing arsenical pigments. It is conceivable that this phenomenon might be realised with naturally-occurring arseniferous materials altogether apart from the intervention of human activities, but hitherto this likely formation of organic arsenicals has not been realised."

Numerous cases are on record of poisoning due to wall-papers bearing arsenical colouring matters, such as Schweinfürth Green (aceto-arsenite of copper) and Scheele's Green (copper hydrogen arsenite); Kirchgasser (*Vierteljahr. gericht. Chem.*, N.F., 9, 96) has described twenty-six such cases. According to Allen (*Organic Analysis*, 4th Ed., Vol. VII, p. 355), Selmi has shown that a volatile arsine, possessing a strong toxic action, is formed by the contact of arsenious acid and albuminous matter; and T. Husemann (*Arch. Pharm.*, 1881) suggested that such a compound was formed from the size or paste used in fixing arsenical wall-paper.

The former worker (F. Selmi, *Gazz. Chim. Ital.*, 1881, 11, 437) described a volatile arsenical compound which gave a crystalline hydrochloride, and which he had found in the urine of dogs that had been receiving small doses of arsenic. The alleged formation of these volatile bodies was said to account for the reported disappearance of arsenic from corpses, but Mario Tonegutti (*J. Chem. Soc.*, 1909, *A.*, ii, 700), investigating the putrefaction of protein substances containing arsenic, declared that it was not accompanied by the evolution of arsenical gas, although small quantities of organic arsenic compounds appeared, these having a basic character and being volatile at 50 to 60° C.

In nearly all the wall-paper cases, the poisonous effects were attributed entirely to the presence in the air of the room of arsenical dust. Fleck (*Z. f. Biol.*, 1873, 8, 444), investigating the presence of arsenic in the air of rooms having arsenical wall-papers, declared that, in addition to arsenical dust, there was present arsenious hydride, which was produced by the action of organic matter (starch paste and gelatin) and moisture on the free arsenious acid contained in the arsenic colour.

N. P. Hamburg (*Pharm. J.*, (3), 1874, [iii], 4, 81) passed the air of a similar room into silver nitrate solution after removing all dust, and found the presence of both arsenic and silver sulphide indicated. H. C. Bartlett (ANALYST, 1880, 5, 81) passed the air with hydrogen containing a little ammonia on to silver nitrate paper, and obtained a dark stain.

Emmerling (*Ber.*, 1896, 29, 2728), investigating a case due to arsenic-containing curtains, declared the improbability of the volatilisation of arsenic by the agency of micro-organisms. This was contested by B. Gosio (*Ber.*, 1897, 30, 1024), who described the action of certain moulds which were able, under suitable conditions, to synthesise volatile arsenic compounds. He found that the most active was *Penicillium brevicaule*; other moulds having a similar action were *Mucor mucedo, Aspergillus glaucus* and *A. virens*. In a later paper (*L'Orosi*, 1900, 23, 361) Gosio described a method of utilising this action of *P. brevicaule* for the detection of small quantities of arsenic in organic materials, relying on the intense garlic-like odour of the arsenical gases evolved. He placed the sample, or a portion of it, upon sliced potato or bread, and sterilised the whole, after which it was inoculated with sterile water containing, in suspension, spores of this particular mould, and then incubated at 37° C. Gosio apparently used this method with success in examining mineral waters, viscera, physiological secretions and minerals.

F. Abba (*Centrbl. Bakteriol.*, 1898, [ii], 4, 806) repeated and confirmed some of Gosio's work, and the test is sometimes described under his name; he found the biological method to be more delicate than that of Marsh. Abel and Buttenburg (*Chem. Centrbl.*, 1900, 1, 428) described several other moulds capable of volatilising arsenic, and stated that they could detect 0·001 mgrm. by Gosio's method. The extreme delicacy of this qualitative test was further confirmed by W. Scholtz (*Chem. Centrbl.*, 1899, ii, 1032), and again by Valerio and Stryzowski (*Chem. Centrbl.*, 1901, i, 63). A. E. Bell (*Pharm. J.*, [iv], 17, 484) and M. Segale (*Z. physiol. Chem.*, 1904, 42, 175) have also investigated certain aspects of this biological reaction, while the necessity for the presence of carbohydrate has been emphasised by Neppi (*Scienza Pratica*, 1908, 1, 82).

G. Markmann (*Chem. Centrbl.*, 1900, ii, 1187) declares that if sulphur or phosphorus be present, the garlic odour is masked; Maasen (*ibid.*, 1902, i, 1245) and O. Rosenheim (*J. Chem. Soc., Proc.*, 1902, 138) point out that compounds of tellurium and selenium are attacked by *P. brevicaule* and other organisms, giving off volatile bodies. In the case of tellurium the odour is similar to that from arsenic; several organisms are known which decompose tellurium and selenium compounds, but not arsenic. Knaffl-Lenz (*Arch. expt. path. Pharm.*, 1913, 72, 224) was unable to find a mould giving volatile compounds with antimony.

Among the species reported to be capable of liberating gaseous arsenic compounds are *Stemonitis* (Biourge, *Étude Monographique*, 1923). According to Thom (*The Penicillia*, 1930, 92), however, Biourge had misunderstood Thom's conception of *P. divaricatum* (Thom) which Depoorter, in 1921, found to be the most active form, enabling him to detect as little as 0·00008 per cent. of arsenic.

Discussing the question of the degree of tolerance of mould fungi for arsenic, Thom (*loc. cit.*, p. 93) reports that in the Bureau of Chemistry of the Agricultural Department, U.S.A., small mould colonies developed on a 0·5 per cent. solution of arsenious oxide exposed to the air for five months, and that a strain allied to *P. purpurogenum* was subsequently isolated from the growth.

This peculiar faculty of liberating volatile arsenic compounds is not confined to the so-called "arsenic moulds." V. Puntoni (*Ann. d'Ig. Roma*, **1917**, **27**, **293**) records that persons taking arsenicals, such as sodium cacodylate, by ingestion, exhale a penetrating odour resembling garlic, which is due to the bacterial decomposition of the arsenic compound.

2. Various conflicting statements have been made as to the exact nature of the arsenic compound volatilised by *P. brevicaule*. G. Markmann (*loc. cit.*) and others refer to it as arsenious hydride, but Biginelli (*Atti Real. Accad. Lincei*, **1900**, [v], **9**, **210**) decided that it was di-ethyl arsine. In this he was supported by Neppi (*loc. cit.*), but Klason (*Ber.*, **1914**, **47**, **2634**) stated that the gas evolved was di-ethyl cacodyl oxide $(AsEt_2)_2O$, and that arsine was never produced.

It was recorded by Gosio (*loc. cit.*) that on passing the evolved gases into a 10 per cent. solution of mercuric chloride in dilute hydrochloric acid, a crystalline mass was formed at the point where the gas entered the liquid. Biginelli (*loc. cit.*) gave the composition of this body as $AsHEt_2.2HgCl_2$. Another worker (*Il Policlinico*; through *Repertoire*, **14**, **88**) declared that this substance was metallic arsenic, and that, by collecting and weighing it, quantitative results could be obtained; this statement appears to lack confirmation.

Most of the published work on this subject is in agreement as to the poisonous nature of the volatilised arsenic compounds; Gosio proved it to his own satisfaction at the expense of some rabbits; but Huss (*Z. Hyg.*, **1914**, **76**, **361**) declared that "the arsenic-containing gas possesses little toxicity."

A survey of the literature available suggests to my mind the possibility that *P. brevicaule* and its allies may volatilise arsenic in more than one form; this would be quite in keeping with the nature of the phenomenon and would account, to some extent, for the apparently contradictory statements of certain of the investigators.

3. Originally it was my intention to see if the biological method could be utilised practically in detecting and determining small quantities of arsenic in organic materials, without any preliminary destruction of organic matter, particularly with reference to arsenic existing in organic combination.

Unfortunately, with the only two cultures of *Penicillium brevicaule* which were tried (they were obtained from the Lister Institute), absolute failure was experienced in producing any mould growth accompanied by liberation of arsenic. On this point the opinion was advanced by one authority that the moulds in question lose their specific property after a time, and require special cultural conditions to restore it.

Attempts were, therefore, made to obtain mould growths on various nutrient media, as well as on foods (raw potato, fish, etc.) in the presence of small and varying amounts of arsenious oxide. In no case was any volatile arsenic compound detected, either by means of mercuric chloride or by the characteristic garlic odour. The matter was dropped at this stage, but two other suggested points were investigated.

The first was whether, in the event of the mould action being enzymic, pepsin or taka-diastase had any similar action. Artificial digestions were carried out with each, in the presence of varying amounts of arsenic, but no positive results were obtained. The second point was raised in the case of *Rex* v. *Greenwood*, when it was suggested by the defence that arsenical weed-killer, sprinkled on a garden path, could result in volatile arsenic compounds being produced by the agency of soil bacteria. Experiments were made with several samples of garden soil, to which arsenic had been added, but no volatile arsenic could be detected.

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Woods Used by the Ancient Egyptians

By KENNETH P. OAKLEY

As no one can hope to have specialised knowledge in all branches of science, it is almost essential for the modern archaeologist to obtain the co-operation of technical experts.

Is it too much to suggest that owners and curators of archaeological collections should have the materials of which their specimens are made scientifically examined, so that the misleading statements, at one time so common on museum labels, might be avoided? The accompanying photomicrographs, illustrating the structure of two of the commonest woods employed by the ancient Egyptians, may be of interest to those engaged in such research on Egyptian materials.

These photomicrographs show sections of specimens in my own collection. The sections were cut and examined for me by Mr. J. C. Maby, then of the Forest Products Research Laboratory (Oxford Branch), by whose kind permission I am able to reproduce them. They illustrate a special application of the technique recently described by him (ANALYST, 1932, 3).

FIG. 1.—A transverse section cut from a wooden model of a building-cradle (used in raising blocks of stone) found in a "Foundation Deposit" under the Temple of Queen Hatshepsut at Dêr el-Baḥarî, and dating from about 1500 B.C. The wood is that of *Ficus sycomorus* (?), which was one of the most important indigenous trees growing in Ancient Egypt. Although this wood was extensively used in Egypt when small lengths only were required, it has serious limitations, and its coarse grain and light spongy texture make it unsuitable for long straight planks or beams. The hulls of many Nile boats in Egypt were made of this wood, cut up into short rectangular blocks and built "brickwise."

FIG. 2.—A transverse section cut from a block of wood which originally formed part of the side of a Xth–XIth dynasty coffin (*circa* 2200–2000 B.C.) found at Dêr el-Baḥarî. The wood is coniferous, and hence must have been imported from abroad. It is, in fact, almost certainly the wood of Lebanon cedar (*Cedrus libani*, Barrel).

FIG. 3.—A transverse section from a piece of coffin wood (probably XIIth dynasty, *circa* 2000 B.C.), which has also been identified as *Ficus sycomorus*.

ANCIENT EGYPTIAN WOODS

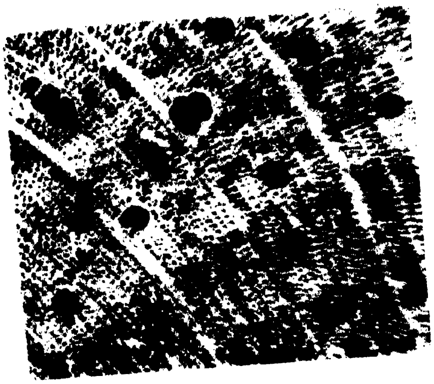
Fig. 1

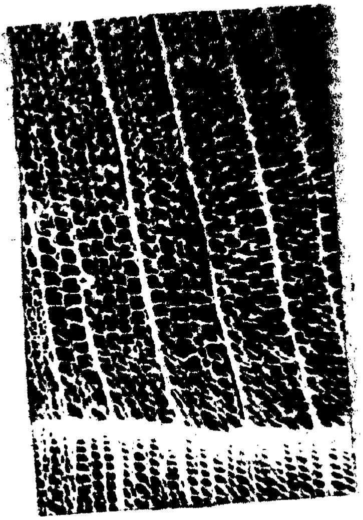
Fig. 2

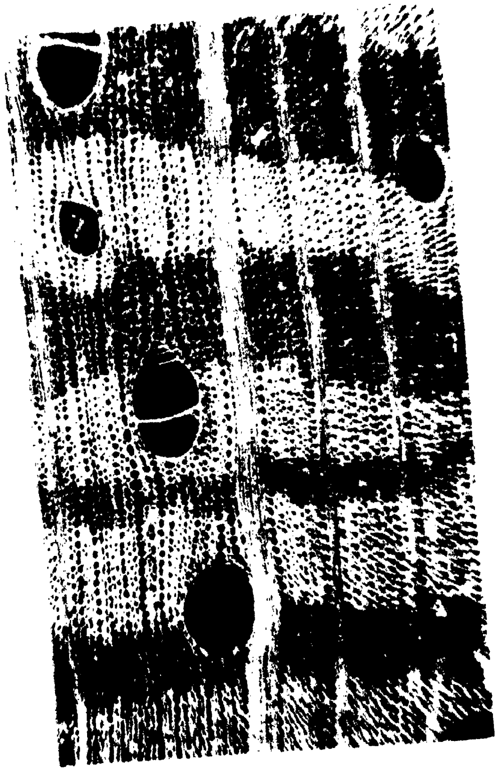
Fig. 3

Fig. 1. *Ficus sycomorus* (?). Cut from near centre of tree. Transverse section × 50 linear.
Fig. 2. *Cedrus libani*, Barrel. Transverse section × 50 linear.
Fig. 3. *Ficus sycomorus*. Cut from near the outside of the tree. Transverse section × 50 linear.

As Professor P. E. Newberry pointed out in his Presidential Address to the Anthropological Section of the British Association, 1923, Lebanon cedar is not the durable and priceless wood that some writers have thought it to be, although it was certainly superior to any wood native to Egypt itself, and hence in ancient times formed relatively valuable timber. The wood is reddish in colour, and has a silky grain. It is apt to shrink and warp badly under some conditions. Nevertheless, it was one of Egypt's most valued imports, because the one thing that the country lacked was large timber. As early as the Ist dynasty coniferous wood (almost certainly *Cedrus libani*) was being shipped from Palestine to the Valley of the Nile, and throughout Egyptian history the trade was continued, with the result that Byblos, the port of the Forest of Lebanon, became one of the chief maritime trading centres on the Syrian coast.

The following is a summary of the identifications of the woods from which the Egyptian specimens in my collection were made, and I am much indebted to Mr. L. A. Boodle, of Kew, to Mr. J. C. Maby and to Mr. B. J. Rendle, of the Forest Products Research Laboratory, Oxford, for their assistance in the identification of these woods.

Wood.	*Object made of the wood.*	*Date about*	*Source of the wood.*
Ficus sycomorus	XIIth dynasty, coffin	2000 B.C.	Egypt.
Ficus sycomorus	XIIth dynasty, tomb statuette	2000 B.C.	Egypt.
Ficus sycomorus	Model building-cradles	1500 B.C.	Egypt.
Cedrus libani	X–XIth dynasty, coffins	2200–2000 B.C.	Lebanon.
Tamarix nilotica (?)	Model mattock, from Dêr el-Baḥarî	1500 B.C.	Egypt.
Acacia seyal or Acacia nilotica (?)	Boning-rod with flax string	1st cent. B.C.(?)	Egypt.
Buxus sempervirens	Mummy labels, with Greek script	3rd–4th cent. A.D.	N. Africa (?).
Tilia, sp.*	Mummy label, with Greek script	,, ,,	Some country north of Egypt.
Fagus sylvatica†	Mummy label with Coptic script	,, ,,	,, ,,

* Lime. † Beech.

A Simple Apparatus for the Rapid Determination of Combustible Vapours in the Atmosphere

BY L. C. McNAIR, B.Sc., AND H. C. GULL, M.Sc.

ASSOCIATED with the industrial use of inflammable organic liquids are frequently their poisonous character and the risks of explosion. It is useful, therefore, to have a simple and rapid method whereby the concentration of the vapour of such liquids present in the atmosphere of a room or tank may be determined with reasonable accuracy. For this purpose the Haldane apparatus (Foster and Haldane, 1905, *The Investigation of Mine Air*, p. 100) has been largely used.

In order to meet the desire for an apparatus which embodies the principle of that of Haldane, but is more portable, the instrument to be described was devised. This matter was brought to our notice some three years ago, and the present modification of the Haldane apparatus is the outcome of experiments made in this laboratory during the last two years.

It consists of two glass vessels of approximately 100 ml. capacity: one of known volume to contain the sample of air under examination (Vessel A, Fig. 1), the other a control vessel, B. In Fig. 1, for the sake of clearness, the manometer and burettes are shown displaced to the right, whereas in the actual apparatus they are in front of vessels B and A, respectively. Both vessels are immersed in a water-bath which is stirred by a current of air. The control vessel, B, is fitted with a stopcock, C, opening to the air, and is connected with the sample vessel by the manometer, M, containing coloured water, and the cock, D. For the construction of the manometer, capillary tubing of approximately 0·5 mm. bore is used, and the two limbs are connected at their lower ends by a piece of rubber tubing bound with copper wire to prevent kinking. A small bulb, of 0·5 ml. capacity, is blown in the upper part of each limb, to minimise the risk of the coloured water being drawn out of the manometer by a considerable difference in pressure between the two vessels.

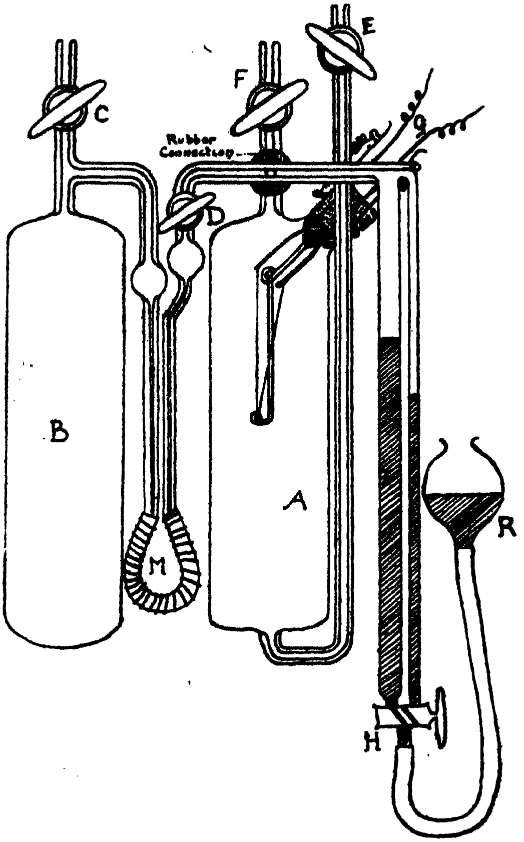

Fig. 1.

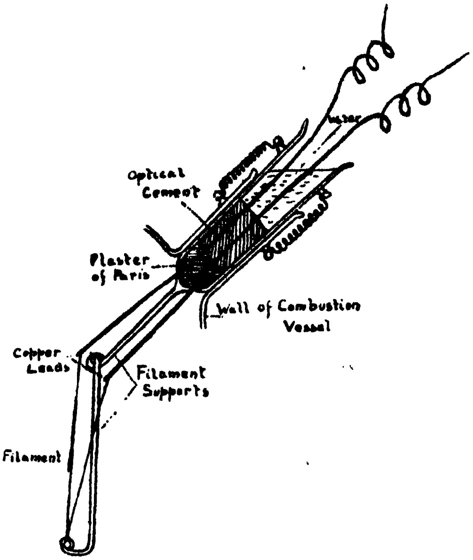

Fig. 2.

At its lower end the sample vessel, A, is fitted with an inlet tube and stopcock, E, and at the top with an outlet tube and cock, F. This vessel is in connection with the manometer and with a graduated burette consisting of two branches; the larger, with a capacity of 5·5 ml., is graduated in tenths of a ml., and the smaller, with a capacity of 1 ml., in hundredths of a ml. A three-way tap, H, at the lower end of the double burette, allows either section to be connected independently with the reservoir, R. Mercury or water may be used in the reservoir and burettes. The overall dimensions of the apparatus are 10 in. × 5 in. × 3 in.

It has been found advisable to have the arrangement for combustion as a separate entity. A side tube, 1 cm. in diameter, is sealed into the upper end of the sample vessel. Into this is ground a glass stopper, G, carrying a platinum filament, together with its supports and electrical connections, by means of which the inflammable vapour in the sample vessel is burned to carbon dioxide and water. Fig. 2 illustrates the construction of this stopper in greater detail. To the lower end of the stopper is sealed a short length of thin glass rod, terminating in a hook from which is suspended another piece of rod to support the centre of the filament. The ends of the filament are twisted round two stout copper wires which pass to the interior of the stopper through two small holes in the glass, one on either side of the support; there they are held in place by a small plug of plaster of Paris, followed by a non-porous layer of shellac cement or sealing wax of high melting point. The remaining space in the stopper, which is open to the air, may be filled with distilled water, to keep the copper wires quite cold in use. Two springs are used to keep the stopper in place, and a little tap grease is used as a lubricant to ensure a gas-tight joint. This arrangement allows the platinum filament to be easily replaced should a "burn-out" inadvertently occur.

In use, it is essential that the insides of both vessels be kept moist. When carrying out an analysis, all taps are opened, and the reservoir, R, is lowered until the liquid level in the burette to be used is near the lower end of the burette. Taps D and H are then closed, and the air under examination is aspirated through the apparatus, by applying suction at F, until the original air in the sample vessel has been replaced. It usually suffices to aspirate about 400 ml. Taps C, E, and F, are then closed, and D and H are opened. The water-bath is well stirred for a minute or so, and the liquid level in the burette is adjusted so that the water levels in the two manometer limbs are equal. The burette reading is noted, and taps D and H are closed. The filament leads are connected with a battery in series with a small variable resistance, and the filament is raised to a dull red heat for five minutes. At the end of this period the current is stopped and the apparatus is allowed to cool for six minutes, the water-bath being stirred meanwhile. Tap H is first opened, and then D, cautiously, and the liquid level in the burettes is readjusted so as to bring the liquid levels in the manometer back to equality. It has been found that the times given are the least that are necessary to ensure satisfactory results. It should be noted that a considerable pressure is developed in A during combustion, and all taps must be closed and be quite gas-tight before switching on the current.

In order to test the apparatus, mixtures of benzene and air, and of hexane and air in known concentration, were prepared and examined in the following way:

A suitable quantity of the liquid solvent was weighed in a thin-walled, sealed glass bulb and dropped into a clean dry bottle of 11,200 ml. capacity, together with 100 ml. of clean mercury. The bottle was fitted with a closely-fitting glass stopper (a gas-tight joint being ensured with a little tap grease), fitted with a three-way tap, and held firmly in position with a clamp. Some two litres of clean air were then pumped into the bottle, the tap closed, and the bottle shaken vigorously until the glass bulb was broken. A small mercury manometer was connected with the bottle and the pressure in it was measured. The bottle was then connected with the inlet tube of the analysis apparatus by means of a short length of glass tube, rubber connections being reduced to a minimum, and the gas in the bottle was allowed to flow through the combustion vessel, replacing the air therein. An analysis was then carried out as described above. The composition of the gas issuing from the bottle was calculated from the weight of solvent used, capacity of the bottle, pressure and temperature of the gas in the bottle, and the barometric pressure. It was found that the inflammable vapour in these mixtures was partly removed by contact with rubber or water. Results of these test analyses are given below.

In blank tests, a contraction of 0·01 per cent. was always obtained. This was due, not to leaks, but, possibly, to the formation of oxides of nitrogen, since, after combustion, these were detected in the air from the combustion chamber. A deduction was made from all observed contractions to allow for this small error.

RESULTS OF ANALYSES

Substance.	Calculated. Per Cent. (by vol.).	Found. Per Cent. (by vol.).	Contraction observed in vessel of 98 ml., less 0·01 ml. ml.
Benzene	1·18	1·18	2·90
,,	0·807	0·816	2·00
,,	0·023	0·022	0·055
Hexane	1·05	1·04	4·56
,,	0·107	0·107	0·470
,,	0·025	0·025	0·110

The results agree with those calculated. Quantities greater than 2·5 per cent. of benzene or 1·2 per cent. of hexane could not be determined, as a contraction greater than 5·5 ml. could not be measured in our burette.

Mixtures rich in inflammable vapour should first be tested in a stout glass bulb, fitted with a stout filament for firing, to see if an explosion is possible.

In conclusion, it may be stated that several forms of this apparatus were constructed and found unsuitable in one respect or another. Among these was an apparatus with a brass combustion chamber, which gave consistently high results, due to interaction between carbon dioxide and the walls of the vessel, in the presence of moisture.

We desire to tender our thanks to the Government Chemist for permission to publish this work.

THE GOVERNMENT LABORATORY,
CLEMENT'S INN PASSAGE, STRAND, W.C.2.

Official Appointments

The Minister of Health has confirmed the following appointment:

Eric Voelcker, F.I.C., A.R.C.S., as Public Analyst for the Borough of Banbury (December 7th, 1931).

The Minister of Agriculture and Fisheries has confirmed the following appointments:

Harold Lowe, M.Sc., F.I.C., as Agricultural Analyst for the Counties of Anglesey and Caernarvon and the County Borough of Chester (February 23rd, 1932).

John Evans, F.I.C., as Agricultural Analyst for Cardigan (February 23rd, 1932).

J. G. Lunt, F.I.C., as Deputy Agricultural Analyst for the County Borough of Leicester (February 23rd, 1932).

Albert E. Parkes, F.I.C., F.C.S., as Agricultural Analyst for West Ham (February 23rd, 1932).

W. H. Roberts, M.Sc., F.I.C., as Agricultural Analyst for the County Borough of Southport (February 23rd, 1932).

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

GASEOUS ARSENIC FROM WALL-PLASTER

On January 19th an inquest was held at Cinderford, Forest of Dean, on the bodies of two children who had died after a mysterious illness. The parents and two other children were also affected.

Professor H. A. Scholberg, of Cardiff University, said that he had made a microscopical and bacteriological examination of the lungs of the boy. He attributed the death to bronchial pneumonia and blood poisoning. In this case the jury returned a verdict of death from "natural causes," and were of opinion that there was not sufficient evidence to show that the arsenic found had contributed to the death.

At the inquest on the girl, Mr. R. H. Ellis, F.I.C., County Analyst, said that he had found arsenic in certain organs of the body (*viz.* intestines, liver, kidneys and lungs), the total amount (as arsenious oxide) being 2·65 mgrms. He had also analysed samples of the wall-paper and of the plaster. In the paper from a dry part of the wall he had found 8·3 parts per million of arsenious oxide; in samples from a part where the mould was most pronounced there were 2·3 parts per million, and in the plaster there were 91 parts. An unused roll of wall-paper, purchased at the same time, contained 4·4 parts of arsenic per million. He had found definite traces of arsenic being given off in gaseous form from the wall that was affected by mould, and it was significant that the arsenic content of the mouldy wall-paper was only half that in a portion of the new paper, and only a quarter of that in a sample of the same paper taken from a dry part of the wall. In his opinion, the arsenic in the paper was present as an impurity, and he attributed the trouble to the plaster, and not to the paper. The arsenic in the plaster, which was composed of coke breeze and cement, would dissolve in the moisture coming through the wall from the bank of soil outside, and the mould would then grow on the paper and would liberate the arsenic in the form of a very deadly organic compound.

Mr. Ellis added that other tests made by him showed that four of the six members of the family had traces of arsenic in their systems.*

The jury returned a verdict that death was due to dysentery and to exposure to arsenic, which was generated in the house in a gaseous form. They added, as a rider, that the house was not fit for human habitation in its present condition, and should be inspected by the Medical Officer of Health before the family were allowed to return to it.

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* Mr. Ellis has informed the Publication Committee that consideration was given to the possibility of the quantity of arsenic found being present without any question of poisoning, but the distribution of the quantities found was also taken into account and considered in connection with the pathological condition of the organs. One of the chief factors which led to the conclusion formed was the fact that the amount of arsenic found in the lungs was greater in parts per million than in any other part of the body, except the large intestine, and this agreed with the condition of the lungs.

The problem of proving the presence of the arsenic in the air was more difficult, and an attempt to detect it by simple aspiration gave negative results. Experiments were, therefore, made by exposing filter papers, saturated with silver nitrate, on the walls of the house, and these were left for 7 and 9 days, respectively. When these filter papers were destroyed, in the usual way, and the amount of arsenic was determined by the electrolytic Marsh test, small mirrors of arsenic were obtained.—EDITOR.

SUMMONS ISSUED UNDER MILK AND DAIRIES (AMENDMENT) ACT, 1922

ON January 9th, 1932, a dairy farmer was summoned before the Reigate (County) Bench for selling milk to which water had been added, proceedings being taken under Section 4, Sub-section 1, of the above Act, instead of under Section 2 of the Food and Drugs (Adulteration) Act, 1928. The samples in connection with which summonses were issued were taken in course of delivery, and contained 8·41 and 8·28 per cent. of solids-not-fat, and 3·49 and 3·89 per cent. of fat, respectively. In the opinion of the Public Analyst, the freezing points of the samples showed that the solids-not-fat were originally high, not less than 9·1 per cent., and indicated that the samples contained not less than 7 and 9 per cent. of added water. Samples of the mixed milk (in two churns) from the herd (24 cows), taken at the farm 24 hours later, were found to contain 9·16 and 9·39 per cent. of solids-not-fat, and 3·73 and 4·39 per cent. of fat, respectively. A conviction was recorded and a fine of £2 was imposed.

Department of Scientific and Industrial Research

REPORT FOR THE YEAR 1930–1931*

The Report of the Privy Council for Scientific and Industrial Research (pp. 1–8) notes the reduction of expenditure effected and deals with the personnel of the Advisory Council, Research Boards and Standing Committees. During the year the responsibility of the British Museum Laboratory has been transferred to the trustees of the Museum. Twenty-six British patents have been applied for, in connection with the various lines of research, and the report of the Research Committee, set up by the Imperial Conference in 1930, is noted. *The Report of the Advisory*

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* Obtainable at Adastral House, Kingsway, W.C.2. Price 3s. 0d. net.

Council (pp. 9–20) covers the history of the growth of the Department's organisation; its contact with industry through the Research Associations, established by firms in an industry or group of related industries, and by the research stations of the Department; the application of new inventions, and general conclusions reached. The next section of the Report is the *Summary of Work* (pp. 21–93), followed by an account of the *Research Associations* (pp. 94–129) and *Appendices* (pp. 130–175), including a list of publications.

SUMMARY OF WORK

NATIONAL PHYSICAL LABORATORY.—The annual report for the Laboratory has been already published (ANALYST, 1931, **56**, 661).

FUEL RESEARCH.—Work on the constitution of coal and on methods for examining it proceeds, and the work in hand includes the study of pitch and its application to briquetting, domestic heating and testing of combustibility of cokes and other solid fuels; internal combustion engines, and tests of various fuels and blends, and development of gas producers for use with motor lorries; the study of pulverised fuel and some aspects of atmospheric pollution, and the production of lubricating oils from coal.

FOOD INVESTIGATION.—The Report for the year 1930 has been published (see ANALYST, 1931, **56**, 531).

THE LOW TEMPERATURE RESEARCH STATION deals largely with gas-storage of ripe fruit. The two gas-stores for English Bramley's Seedling apples have proved so successful that others are being opened.

Retarding the Ripening of Fruit.—Bananas have been treated for retarding ripening. It has been shown that acetaldehyde is a normal intermediate product in the breakdown and oxidation of sugar to carbon dioxide and water in plant tissues generally, and in over-ripe fruit partial inactivation of the respiratory mechanism results in accumulation of acetaldehyde. Also, by packing the fruit in an atmosphere containing a regulated amount of acetaldehyde, the breakdown of the sugar is thrown out of its normal course.

CANNING.—The problems connected with corrosion of tin plate cans by fruit juices and syrup have been investigated (see ANALYST, 1931, **56**, 315), and the prolonging of the canning season for soft fruits and vegetables by cold storage is suggested as applicable to many products. The colour and flavour of peas can be preserved by parboiling or blanching in water and then freezing and storing indefinitely at $-20°$ to $-10° C$.

PIG PRODUCTS.—The smoking of bacon has been found to retard the onset of rancidity.

TORRY RESEARCH STATION.—CARBOHYDRATE METABOLISM OF FISH.—The nature of vitamin *A* present in the fats of fish and the colour test for it are being studied, and the claims made by Mittelmann, namely, that the oil prepared from fresh cod livers autoclaved in sealed tins did not, on first opening of the tins, respond to the antimony trichloride test, but recovered its chromogenic power on standing, have been investigated and partly substantiated.

DITTON LABORATORY.—The distribution of temperature in a mass of 110 tons of fruit, when refrigerated in different ways, is being mapped. Isolation of the volatile substances given off by apples during storage has been found to be beset with technical difficulties, but is being attempted, and the nature of the waxy coating on apples is also being investigated.

FOREST PRODUCTS RESEARCH.—Among much other work, the conclusions arrived at by the International Conference on Standardisation of Wood Preservatives (ANALYST, 1931, **56**, 127), wherein it was agreed that wood block tests are more likely to give a true value for the toxicity of a preservative than agar tests, have resulted in certain standard methods being worked out in co-ordination with other research institutes, the first step being the choosing of a single vigorous strain of *Coniophora cerebella.*

CHEMICAL RESEARCH.—CORROSION.—In this section quantitative measurements have been extended to the corrosion of iron and mild steel when immersed in salt solutions saturated with oxygen, and determinations have for the first time been made on the rate of the hydrogen evolution from steel in potassium chloride solutions. Exploratory work on the protection of magnesium alloys has involved an examination of more than 500 coatings, from which 12 of the more promising have been selected for further trials. Among such selected coatings were those containing a chromium basis derived from either chromic acid or an alkali chromate. These earlier experiments were followed by the important discovery that protective films of selenium are produced when sheets of light magnesium alloys are immersed in acidified solutions of selenium compounds (selenious acid, sodium selenite, etc.). Such selenium films exhibit a noteworthy resistance to intermittent spraying with salt water.

LOW-TEMPERATURE TAR.—The presence of anthracene and its homologues has been confirmed in the anthracene fraction of low-temperature tar, and the new 2:3:6:7-tetramethylanthracene and the corresponding tetramethylanthraquinone have been synthesised, the former being identified in the low-temperature tar. Homocatechol, iso-homocatechol, resorcinol and quinol have also been identified. To the methods used for separating tar constituents has been added distillation of the least volatile neutral oils and phenols by means of high-vacuum plants. At temperatures not above 120° C. the greater part of the crystalloid portion of these fractions distils over, leaving the resinenes and resinols.

CHEMOTHERAPY.—Two promising indications of therapeutic activity have been revealed by a series of fluorene derivatives containing arsenic, and a new group of arsenicals analogous to tryparsamide.

BRITISH MUSEUM LABORATORY.—*Removal of Stains:* The value of chloramine-T for removing "foxed" and other mildew and mould stains from water colours has been confirmed, and vinyl acetate seems likely to be a valuable strengthening element for porous and friable material.

Among the antiquities from Ur of the Chaldees was a silver dish which has been renovated by a solution of citric acid, still the most efficient treatment for bronze and silver objects alloyed with copper.

Other sections of the Report deal with *The Geological Survey and Museum of Practical Geology ; Building Research ; Steel Structures Research ; Electro-Deposition ; Water Pollution : Radio Research ; Dental Investigation ; Illumination ; Lubrication ; Fabrics ; Geosophysical Survey ; Atmospheric Pollution ;* and *X-ray Analysis of Crystals.*

RESEARCH ASSOCIATIONS

Among the subjects dealt with are:

RESEARCH ASSOCIATION OF BRITISH PAINT, COLOUR AND VARNISH MANUFACTURERS.—With the co-operation of the British Colour Makers' Association a table of fastness has been prepared, which is rapidly being accepted by the industry as a basis of colour evaluation of pigments, and it is claimed that no difficulty will be found in correlating results with those obtained under other defined conditions.

Value of Iron Oxide as Pigment.—An investigation of the precipitated iron oxides shows that the value of iron oxide as a pigment depends on the colour-staining power and other factors (described collectively as paint-making property), depending chiefly on the degree of reactivity between pigment and oil medium. A series of products obtained by heating precipitated iron oxides at different temperatures for different times was examined by *X*-ray methods, and it was shown that the structure developed by the oxide is very sensitive to small changes in degree of heat treatment, and that, up to a point, these are correlated with pigment property.

Lithopones, mechanical mixtures of barium sulphate, titanium oxide and the co-precipitated products have also been examined; and although the *X*-ray patterns of the mechanical and co-precipitated mixtures do not differentiate between these products possessing very different painting properties, the figures are possibly confused through growth or diminution of crystal size as a result of heating.

BRITISH COTTON INDUSTRY RESEARCH ASSOCIATION.—An observation likely to be practically important is that certain fast colours, themselves unaffected in shade during bleaching, are capable of inducing very rapid attack by the bleach liquor of the cotton on which they are dyed, so that in a bleached shirting or other cloth the stripe dyed with such a colour rapidly disintegrates in wear, if not before. Much work on the re-classification of dyestuffs is involved in the light of such information.

WOOL INDUSTRIES RESEARCH ASSOCIATION.—With mixtures of cellulose, leather, rubber and wool, all in suitable form, products resembling leather were produced, and after the preparation of bulk samples, their uses for gloves, boot uppers, leather coats, etc., are being explored. Although a special fabric treatment is involved, wool has been found particularly suitable for such purposes.

BRITISH LAUNDERERS' RESEARCH ASSOCIATION.—Strongly adhering dirt particles are found to be those which, in minute form, are adsorbed on the fibre surface, and not those attached to the fibre by grease. Grease, except when present in large quantities, presents no special difficulty in removal; but for such articles as butchers' or engineers' overalls it is probable that an organic solvent, suspended in a dilute solution containing only just sufficient of an emulsifying agent, will prove helpful. Under suitable conditions the solvent will be deposited only on the greasy or oily areas of the immersed fabric. "Breaking emulsion" methods of treatment may prove economical in the cleansing of such fabrics.

RESEARCH ASSOCIATION OF BRITISH FLOUR MILLERS.—New crop wheat examination is now a permanent feature of the work. Two Reports have been issued, summarising 6 years' study of baking methods, including relations between yeast percentage and time and temperature of fermentation, etc. The importance of fermentation time and tolerance of a flour is emphasised. Methods of determining flour ash, and hydrogen-ion concentration have been improved, and one for finding the hydrogen-ion concentration of dough has been developed, as well as one for measuring the rate of movement of water through wheat. The factors producing "low-gradeness" in flours, and the part played by oxidation on storage, have been studied.

BRITISH ASSOCIATION OF RESEARCH FOR THE COCOA, CHOCOLATE, SUGAR, CONFECTIONERY AND JAM TRADES.—*"Bloom" on chocolate* may be due to formation of a film of minute crystals of cocoa butter, or to crystals of sugar. The methods found for preventing fatty bloom have been successful, both for ordinary chocolates and those with nutty or fatty centres, although, in the latter case, an appreciable cost is added to manufacture.

BRITISH FOOD MANUFACTURERS' RESEARCH ASSOCIATION.—The dominant factor influencing the formation of patchy separation of liquid or fat, and appearance of air spaces and films in potted meat and fish pastes has been found. The closing of paste jars under vacuum was found to remove entirely the greyish discoloration due to the action of residual air, and the purplish discoloration on food in glass containers has been traced to contamination with minute quantities of metals. The causative agent of green discoloration of cooked pickled foods has also been investigated, and methods are suggested for overcoming the discoloration of sausages on exposure to air. D. G. H.

Connecticut Agricultural Experiment Station

ANNUAL REPORT FOR THE YEAR 1930*

THIS Station was the first Agricultural Experiment Station in U.S.A. to be officially charged with food control work by the State legislature. The present law, enacted in 1907, was preceded by a comprehensive and practical statute, passed in 1895, which aimed at preventing adulteration of foods generally. Under this old law the first food report was issued by the Station in 1896. Similar duties were imposed upon the Stations in Kentucky in 1898, in North Dakota and Wyoming in 1903, and in Maine in 1905. Prior to 1895 there were a few special laws governing the manufacture and sale of certain foods, notably vinegar, butter and molasses.

The revision of the food law, made in 1907; contemplated chiefly an inclusion of drugs in the scope of inspection and control, and for the last twenty-three years the annual report on foods has included also an account of drug inspection.

Most of the samples examined are submitted by the Dairy and Food Commissioner, although the Station may, and does, examine samples of both foods and drugs collected by its own agent. In all cases, however, instances of adulteration or misbranding are reported to the Commissioner for corrective action as required by law.

Among the points of interest dealt with by Dr. E. M. Bailey in the present report are the following:

CARBONATED BEVERAGES, ETC.—The provision of the carbonated beverage law, requiring not less than 5 per cent. of sugar in beverages of this type, is always met, and generally exceeded. Failures to declare artificial colours and flavours in beverages where such ingredients are used are rare. Saccharin is seldom found. A number of beverages sold under distinctive names, "Pepsi-Cola," "O. C. Kola," "Coca Cola," and "Braser," contained caffeine in approximately the proportions found in tea infusions, as ordinarily prepared.

CHERRY CIDER.—A product was rather widely sold during the past season under the name of "cherry cider." Artificial colour and flavouring material and a benzoate were regular constituents of the samples examined. In one instance the base of the product appeared to be apple cider to which colour and flavour had been added to simulate the character of cherry.

ORANGE JUICE.—The emphasis placed upon the nutritional advantages of fruit juices has resulted in a large increase in consumption of drinks consisting wholly, or in part, of fruit juice, more especially orange juice. In many instances orange juice is prepared in the presence of the customer and the genuine character of the beverage is unquestioned, but when served from stock solutions the consumer may receive a beverage considerably diluted as regards actual fruit juice. This is well illustrated by the following comparative analyses. Sample 1 is genuine orange juice prepared in the presence of the inspector, whilst samples 2 and 3 are so-called "orange juice," considerably diluted and fortified with sugar and citric acid, and artificially coloured. Analyses are on filtered juice, and are in terms of grms. per 100 c.c.

	1 (genuine).	2 (diluted).	3 (diluted).
Solids	9·40	—	—
Sucrose	4·36	14·51	14·67
Invert sugar	3·32	0·82	0·94
Total sugars	7·68	15·33	15·61
Acidity, as citric acid ..	0·76	0·99	0·97
Ash	0·41	0·08	0·07
Nitrogen	0·052	—	0·017

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* *Bull.* No. 329, 1931.

The characteristics of genuine orange juice are seen to be a relatively high ash and a considerable amount of invert sugar. The sugar distribution in the artificial products will, however, vary, according to the degree of acidity and the length of time that the acid has had an opportunity to act upon the sucrose present. The chief characteristic of the genuine juice is the ash content, which itself is further characterised by its potassium and phosphorus content, in the above cases undetermined.

The proportion of orange juice which should be present in a beverage not claimed to be entirely juice, but laying stress on orange juice content, is not a matter of concordant opinion or practice at the present time. Some State Regulations allow as little as 5 per cent., whilst others require 15 per cent. It would appear that the higher figure is more nearly in accord with what the consumer may reasonably expect in a beverage such as orangeade. This proportion might, or might not, hold for other fruit juices, according to the character of the fruit in question.

Since orange juice, as ordinarily prepared by reaming or other means accomplishing a similar result, contains some pulp, abuses may arise from the inclusion of excess of pulp, and thus create a false impression of fruit juice content.

Considerable attention has been given to the problem of a fair and rational classification of carbonated and still beverages, both by state control officials and by the Standards Committee, but conflicting trade practices and other difficulties have thus far prevented any satisfactory solution to the question.

COFFEE, ETC.—A sample of "Café des Invalides," a product labelled as containing about 7/8 coffee, the remainder being other vegetable substances, was examined. The addition of non-coffee material is designed, in part, to reduce the caffeine content below that of ordinary coffee. A mechanical separation of the ingredients on the basis of 1 grm. showed 0·892 grm. of coffee, 0·092 grm. of vegetable material, which appeared to be pea hulls, and 0·016 grm. of chicory. The caffeine content was 1·10 per cent. The label declaration of 7/8 coffee is borne out by the examination of the product.

Yermat.—A sample of *Yermat*, prepared by The Yerba Maté Corporation of Chicago, was submitted for analysis. This is a carbonated infusion of the dried leaves of Yerba Maté (*Ilex paraguayensis*), sweetened, and flavoured with an essential oil. It contained 8·5 per cent. of sugar and 4 mgrms. of caffeine in each 100 c.c. of solution. The leaves of this plant, sometimes called Paraguay tea, are used in the preparation of an infusion largely consumed in South American countries as a beverage.

IMITATION MAPLE FLAVOUR.—One sample of imitation maple flavour was submitted by the Dairy and Food Commissioner. The brand name was *Elpam*. The accompanying literature showed plainly the imitation character of the product, but the identity of the flavouring principle was not established. An attempt was made to isolate choline and trigonelline by the method of Jahns (*Ber.*, 1885, **18**, 2518) to show the presence of fenugreek, but, although the presence of organic bases was indicated, they were insufficient in quantity to make isolation and identification possible.

SAUSAGES.—Five samples of Frankfurt, and one of Bologna, sausages were examined, and four were found to be illegal because of undeclared cereal or cereal in excess of 3·5 per cent.

In the manufacture of sausage it is permissible to use 3 per cent. of water or ice, and somewhat more in the case of those types of sausage which are smoked or cooked; but in no case should more water be introduced than is necessary to facilitate satisfactory manufacturing processes or to make the products palatable. In the instance of Frankfurt sausages, for example, 10 per cent. of added water appears to be an acceptable margin in control practice.

A study of the ratio of water to protein in the cuts of meat generally used in sausage making indicates that the proportion is 4 to 1. The procedure for estimating excess moisture is to determine total moisture and nitrogen in the samples. The nitrogen, multiplied by 25 (basis of $N \times 6{\cdot}25 =$ protein), should not be exceeded by the total moisture in the sample by more than 3 per cent. in the case of pork sausage, or by more than 10 per cent. in sausage of the Frankfurt type.

Samples of Frankfurt sausages, submitted by a local packer, afforded an opportunity to try this method and to check our results in some cases with those obtained in other control laboratories. Eight samples were analysed. The uncertainty in comparing results from different laboratories hinges particularly upon lack of evidence that the samples submitted to the several laboratories were sufficiently alike in composition to make strict comparisons. In one case of disagreement, results calculated to the water-free basis, showed that the solids in the two samples worked upon were substantially different in amount. If the uniformity of samples is assured, the other sources of disagreement are differences in methods used. Results for nitrogen should be satisfactorily close, but moisture may vary according to the procedure followed. In our work, drying for 16 hours at 100° C. in an air-oven was found to compare very closely with results obtained by the Bidwell-Sterling distillation method.

One sample in this series, upon which results for added water from three laboratories are available, shows data as follows:—This laboratory, 9·3 per cent.; laboratory A, 11·3 per cent.; laboratory B, 10·7 per cent. The results (this laboratory) in detail are as follows:

	Per Cent.	Per Cent.	Per Cent.		Per Cent.
Water (drying oven) ..	60·2	59·8	59·4	avg.	59·8
(distillation method)	—	—	—		59·6
Nitrogen	2·01	2·03	2·03	avg.	2·02
Protein ($N \times 6{\cdot}25$).. ..	—	—	—		12·63
Protein × 4	—	—	—		50·5
Added water (59·8—50·5)	—	—	—		9·3

On the basis of these data it would appear that only one of these results would raise any question whether the limit of 10 per cent. of added water had been exceeded. How strict an interpretation can be placed upon the margin between the 10 per cent. tolerance and the highest result reported, *viz.* 11·3 per cent., will depend upon what evidence is available that the sample is representative of the batch involved, and on the coefficient of error in determining moisture and nitrogen in the laboratory concerned.

MARKET MILK.—The large proportion of samples (214 of 785 examined) found to be, in part, skimmed, is explained by the fact that many were found in places where milk was dispensed either by dipping, or from quart bottles rather than from individual service bottles. The law requires that milk, when served by any hotel, restaurant, lunch room, fountain or any other place of public entertainment, shall be served in the original bottle, the cap of which shall not be removed except in the presence of the customer. Commenting upon this provision of the statutes, the Dairy and Food Commissioner says in his biennial report: "So gratifying are the results of the original or individual bottle law that a sampling campaign is now being carried on to demonstrate, particularly to the 'fountain' interests, the extremely low quality of milk used in mixed drinks. Hundreds of samples indicate that milk so used contained much less than the legal standard of butter fat."

It was with this in mind that the inspection was extended by the Commissioner to include tests for milk fat in milk drinks dispensed by "fountains." This inspection was confined, however, to so-called "milk shakes," in the preparation of which, other materials are not added in amounts sufficient to reduce the fat content of the drink substantially below that in the milk used in its preparation.

Sixty-five samples were examined, which may be classified as follows:—Below 3·25 per cent. of fat (legal standard for milk), 39; above 3·25 per cent. of fat, 26. In the first group, the fat content ranged from 0·9 to 3·2 per cent., and averaged 2·5 per cent. In the second group, the range was from 3·3 to 7·2 per cent., and the average 4·0 per cent. High percentages of fat indicate the use of top milk. There is no official definition of what constitutes the article known as a "milk shake," but it has been ruled that skimmed milk should not be used in the preparation of drinks sold as chocolated milk or milk chocolate and, by analogy, it would appear that whole milk should be used in the preparation of milk shakes.

SALAD DRESSING, MAYONNAISE.—Mayonnaise salad dressing is essentially an oil dressing further characterised by varying amounts of egg-yolk or whole egg, and contains vinegar or lemon juice and seasoning materials. The U.S. Department of Agriculture, in its standard for this product, specifies for the major ingredients not less than 50 per cent. of oil and a percentage of egg-yolk and oil together of not less than 78.

The estimation of the egg content in materials of this sort is made upon the basis of accepted average values for lipoid phosphoric acid, which is present in egg-yolk, but absent or negligible in the white. It is evident that the application of a uniform factor for the estimation of the egg content of various brands of market mayonnaise dressings involves necessary reservations. The accepted value for the lipoid phosphoric acid content of whole dry egg is 1·38* per cent., and for dry egg-yolk 1·78* per cent. Assuming 25 per cent. of solids for fresh whole egg, and 50 per cent. of solids for fresh egg-yolk, these percentages become 0·35 and 0·89, respectively.

The following table gives the results of a few typical analyses:

ANALYSES OF MAYONNAISE DRESSINGS

Manufacturer and brand.		[illegible]	Solids.	Ash.	Protein ($N \times 6·25$).	Carbohydrate, including fibre, by diff.	Fat (Roese-Gottlieb	Salt.	Acidity (as Acetic acid).	Lipoid P_2O	Distribution of egg and oil, estimated. Egg-yolk, fresh.	Oil.	Oil and egg-yolk.
Booth, *Booth's*	none	+	92·33	0·87	0·88	3·21	87·37	0·68	0·29	0·020	2·25	86·62	88·87
Duke Products Co., *Duke's*	none	–	87·91	1·21	1·50	0·82	84·38	1·05	0·55	0·039	4·38	82·92	87·30
Easton, *Easton's* .	nône	+	86·29	1·24	1·75	2·46	80·84	0·91	0·49	0·060	6·74	78·60	85·34
Heinz, T. H., Co. *Heinz*	none	–	86·44	1·04	1·88	0·00	83·52	0·76	0·34	0·060	6·74	81·27	88·01
Ivanhoe Foods, Inc., *Shady Lane* . .	present[1]	+	72·58	1·71	1·75	5·17	63·95	1·40	0·58	0·056	6·30	61·85	68·15
Kraft-Phoenix Cheese Corp., *Kraft* .	none	+	85·76	1·18	1·44	1·99	81·15	0·92	0·33	0·052	5·84	79·20	85·04
Leggett, *Premier* .	none	+	63·82	3·06	3·75	1·73	55·28	1·83	1·37	0·138	15·50	50·11	65·61
Preston Market Co., Inc., *Premar* .	none	–	87·60	1·43	1·25	3·09	81·83	1·15	0·43	0·019	2·13	80·60	82·73
Swift & Co., *Gem* .	none	+	79·17	2·07	1·44	5·43	70·23	1·71	0·66	0·027	3·04	69·22	72·26

[1] Corn starch declared.

EXAMINATION OF ANIMAL TISSUE FOR ARSENIC.†—An examination made recently, when it seemed advisable to utilise all the procedures noted, is recorded here because of its interest from the standpoint of closely agreeing analytical results.

The material was finely comminuted to insure reasonable uniformity of sample. A portion was first subjected to the Reinsch test and a copious steel grey deposit on copper foil was obtained. Thin strips of the foil were then introduced into a capillary tube, and, by careful heating, a sublimate was formed which revealed the characteristic octahedral crystals of arsenic trioxide when viewed with a microscope. The crystals may be seen distinctly in the capillary tube, and it is not necessary to resort to manipulation to obtain them on a slide before making the microscopic examination. This test alone establishes a strong presumption of the presence of arsenic, but, since antimony deposits as a film on copper foil, and yields a sublimate which, although generally amorphous, may consist of, or contain, octahedral crystals, further tests to identify arsenic are necessary. This test was carried out on the original materials, without destruction of organic matter, the copper foil being placed in a suspension of the tissue in water acidified with hydrochloric acid. A weighed quantity of material was then boiled with sulphuric acid and nitric acid until organic matter was destroyed, and the solution was made up to definite volume with water. Aliquot parts were taken for subsequent determinations.

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* Hertwig, *Proc.A.O.A.C.*, 1924, 8, 2, 118.

† By C. E. Shepard and E. M. Bailey.

The Gutzeit test furnishes qualitative evidence of arsenic, and the method may also be conducted on a quantitative basis. Aliquot parts from each of the solutions, representing 0·4 grm. of original material, were used. Freshly prepared and standardised mercuric bromide strips were used in measuring the arsenic liberated. This test was conducted substantially as described by Sanger and Black (*Amer. Acad. Arts and Sciences*, 1907, **43**, 297–324). Freedom of all reagents used from contamination with arsenic was established by suitable blank determinations. Duplicate determinations, representing two separate portions of original material, gave 35μ of arsenic (as trioxide), or 1·75 grains calculated to the basis of the original weight of material submitted (2 lbs. 14 ozs.).

The Ramberg method, described by Cox (ANALYST, 1925, **50**, 3), has been found to be reliable for the determination of small amounts of arsenic in animal tissues, and was used in this laboratory in the investigation of experimental mixtures of arsenical spray materials (*Conn. Exp. Station Bull.*, 1926, **278**). Arsenic was distilled and titrated with standard potassium bromate solution, 1 c.c. of which was equivalent to 0·00037 grm. of As_2O_3. The quantity of arsenic found by this procedure, when calculated to the basis of the original weight of material submitted, was 1·69 and 1·80 grains of As_2O_3, obtained in duplicate determinations.

Finally, the Marsh test, as modified by Berzelius, was applied. A characteristic mirror was obtained, the weight of which, calculated to its equivalent in As_2O_3 and to the basis of the original material submitted, was 1·32 grains. This figure is, no doubt, less accurate than those obtained by the other two methods employed. The mirror is probably not of uniform composition; the darker portion of the mirror is metallic arsenic; but the lighter, brownish portion, according to Rettgers (Peterson, Haines and Webster, "*Legal Medicine and Toxicology*," **2**, 231), consists of suboxide, As_2O, and hydride, AsH. The spot test with silver nitrate and nitric acid, the characteristic yellow sulphide and the odour of arsine, confirmed the identity of arsenic.

To summarise the quantitative results, the amounts of arsenic found were as follows:

By Gutzeit method	1·75 and 1·75 grains
,, Ramberg method	1·69 and 1·80 grains
,, Marsh-Berzelius method	1·32 grains.

Vitamin Standards

REPORT OF THE PERMANENT COMMISSION ON BIOLOGICAL STANDARDISATION*

THE International Conference on vitamin standards was presided over by Professor E. Mellanby, and was attended by representatives of Denmark, France, Holland, Germany, Great Britain, Norway, Sweden, and the United States of America. The British participant was Professor J. C. Drummond.

It was the general opinion that, in the present state of our knowledge, only vitamins *A*, *D*, *B*, (also known as vitamin B_1), and *C* could be profitably discussed in connection with standardisation.

I. THE FAT-SOLUBLE VITAMIN *A*

(*a*) INTERNATIONAL STANDARD.—*The Conference recommends that carotene be accepted as an international provisional standard of reference for vitamin* A, *and that a selected sample of cod-liver oil be held in view as a possible secondary standard.*

(*b*) MODE OF PREPARATION.—It was decided that the information available does not yet justify the selection of one isomer of carotene as a standard. The similar biological activity of the two isomers that have recently been described is further justification for adopting as the provisional international standard a mixture prepared in an approved manner.

It was decided to employ a preparation of carotene made from carrots by Willstätter's method and purified by recrystallisation by the method described in the memorandum issued by the Department of Biological Standards, National Institute for Medical Research, London (Appendix, p. 76), until the melting-point determined is above 179° C. It was suggested that preparations should be made in various countries and despatched immediately and with all necessary precautions against decomposition to the National Institute for Medical Research, London, where they will be mixed to form a uniform preparation by the most suitable method. The details of this final purification are to be left to the discretion of the authorities of the National Institute. It was suggested that original preparations of, say, 4 to 5 grms., might be made in the following institutions:

Department of Physiological Chemistry, University of Amsterdam.
"Laboratoire de physiologie de la nutrition, École des Hautes Études," Paris.
"Tierphysiologisches Institut," Leipzig.
National Institute for Medical Research, Hampstead, London.
Department of Agricultural Chemistry, University of Wisconsin, U.S.A.
Biochemical Department, University of Stockholm, and "Institut für Organische Chemie der Universität," Zürich.
School of Hygiene and Public Health, Johns Hopkins University, Baltimore, U.S.A.

(*c*) PLACE OF PREPARATION.—It was decided that the National Institute for Medical Research, London, acting for this purpose as the *central laboratory on behalf of the Health Organisation of the League of Nations*, should be asked to undertake the final preparation of the sample of carotene to be used as the international standard for vitamin *A*.

(*d*) MODE OF DISTRIBUTION.—It was considered desirable that, as far as possible, the standard preparation should be distributed to workers through the appropriate official institution in each country, preferably that now responsible for the distribution of similar biological standards. The material should be sent out in tubes of 10 mgrms., as described in the Appendix, p. 76.

(*e*) DEFINITION OF UNIT.—The unit of vitamin *A* recommended for adoption is the vitamin *A* activity of 1γ (0·001 mg.) of the international standard.

Note.—Daily doses of about 3γ to 5γ of the international standard, when administered to young rats suitably prepared on a vitamin *A*-deficient diet, have been found adequate to restore growth and to cure xerophthalmia.

(*f*) PERMANENCE OF THE STANDARD.—The Conference recommends that this international standard and unit be accepted provisionally for two years.

(*g*) SUBJECTS RECOMMENDED FOR FUTURE INVESTIGATIONS.—It is highly desirable that, during the provisional period, further investigations of the standard should be made regarding the stability of the carotene preparation, both when sealed in the original tubes and after it has been removed and dissolved for biological testing. In the latter connection, emphasis is laid on the importance of minimising contact with air or oxygen of the solutions used for animal feeding. It is recommended that they be always stored in an inert gas and at low temperature.

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* League of Nations Health Organisation. Report of Conference on Vitamin Standards, held in London from June 17th to 20th, 1931. Official Number C.H. 1056(1). Annex IV, CH. 1055(1). London: George Allen & Unwin, Ltd. Price 1s. 6d.

It will be of great value if investigators submit to the League of Nations Health Organisation observations on the stability of the preparation, its behaviour in various solvents and under different conditions of storage, and any other information bearing on its use as a biological standard. The use of suitable "antioxidants" ("*antioxygènes*" in French) should, in particular, be studied.

(*h*) BIOLOGICAL METHODS FOR ESTIMATION OF VITAMIN *A*.—It was decided not to recommend any one particular method of conducting the biological assay, but to invite members of the Conference to submit to the League of Nations Health Organisation their observations on the value of the methods they have been using.

It is recommended that further attention be given to the methods based on the curative action of carotene for xerophthalmia and other lesions characteristic of vitamin *A* deficiency, as well as to those based on increase in weight.

(*i*) SELECTED SAMPLE OF COD-LIVER OIL FOR USE AS A POSSIBLE SECONDARY STANDARD.—It is recommended that a supply of an approved sample of cod-liver oil be obtained with the object of making a series of comparative tests to determine its suitability as an alternative standard. The Conference is informed that the United States Department of Agriculture is making arrangements for such a standard substance to be available in the United States during the coming year.

It was decided to ask the United States Department of Agriculture to obtain sufficient supplies of the oil for distribution in order to enable investigators of other countries to assay this oil in terms of the international unit of standard carotene. It is hoped thus to obtain evidence regarding the stability of vitamin *A* in cod-liver oil as affected by conditions and time of storage.

III. THE ANTIRACHITIC VITAMIN *D*

(*a*) INTERNATIONAL STANDARD TO BE ADOPTED AND ARRANGEMENTS FOR CONTROL.—*The Conference recommends that the standard solution of irradiated ergosterol at present issued from the National Institute of Medical Research, London, be adopted as international vitamin D standard for the next two years.*

If within this period it should become necessary, owing to threatened exhaustion of the present supply, to replace this solution by a fresh standard, the equivalence shall be determined by experts of different countries who have had the opportunity of comparing the proposed new standard with the one at present issued. It is suggested that the following Institutions, among others, be invited to co-operate in those tests:

"Allgemeines Chemisches Laboratorium," Göttingen.
"Tierphysiologisches Institut," Leipzig.
Food and Drugs Administration Laboratory, Department of Agriculture, Washington, D.C.
Biochemical Department, University of Stockholm.
Department of Agricultural Chemistry, University of Wisconsin.
School of Hygiene, Johns Hopkins University, Baltimore.
"Laboratoire de physiologie de la nutrition, École des Hautes Études," Paris.
Pharmaceutical Society, London.

(*b*) METHOD OF PREPARATION.—1. It is recommended that, in the preparation of the solutions of irradiated ergosterol, used as standards of reference for vitamin *D* (or as sub-standards), irradiation with ultra-violet light shall be done in ethereal solution in the absence of any appreciable traces of oxygen, and the solution should be kept meanwhile in rapid motion. The conditions of exposure should be such as to transform between 30 per cent. and 80 per cent. of the ergosterol. The solution of the product and further dilutions shall be made in a stable unsaturated natural vegetable oil, which has given a negative test for vitamin *D*.

2. The standard solution of irradiated ergosterol at present issued from the National Institute for Medical Research, London (Standard Solution III), was, however, prepared as follows, in January, 1929:

> A 0·1 per cent. solution of the ergosterol in absolute alcohol was exposed for half-an-hour in a silica cell, 1 cm. thick, to the unfiltered radiation from a K.B.B. (Kelvin, Bottomley and Baird) mercury vapour lamp, taking 2·5 amperes and 125 volts at atmospheric pressure, at 15 cm. distance from cell to lamp. The resulting solution was mixed with a little olive oil, and then evaporated at 45° C. at a low pressure to remove the alcohol. The concentrated oily solution thus obtained was diluted with pure olive oil to give a concentration corresponding with 1 mgrm. of the original ergosterol in 10 c.c. of olive oil at 18° C. The olive oil used was tested for stability and gave a negative test for vitamin *D*.

The additional larger quantity of standard (prepared January, 1931), which is available for distribution later if required, was prepared with observance of the general conditions indicated under 1.

(*c*) MODE OF DISTRIBUTION.—The National Institute for Medical Research, London, *acting for this purpose as the central laboratory on behalf of the League of Nations Health Organisation,* shall distribute to each country wishing to use the standard a sufficient quantity of the solution to enable the standard to be effectively applied according to the conditions in the particular country. Such quantity shall be supplied only to a central institution nominated for the purpose by the country concerned, which will be responsible for the distribution either of the portion of international standard solution received or, wherever possible, of an equivalent substandard prepared by comparison therewith.

(*d*) STABILITY OF THE INTERNATIONAL STANDARD.—The stability of the standard solution at present issued from the National Institute for Medical Research, London, has proved satisfactory on the results of tests over a period of two years, when preserved at or below 0° C., with exclusion of air.

(*e*) DEFINITION OF UNIT.—The unit of vitamin *D* recommended for adoption is defined as the vitamin *D* activity of 1 mgrm. of the international standard solution of irradiated ergosterol.

Note.—The international standard solution has been prepared to have such potency that approximately 1 mgrm. thereof given daily to a rachitic rat for eight successive days will produce a wide line of calcium deposits in the metaphysis of the proximal ends of the tibiae and of the distal ends of the radii.

(*f*) PERMANENCE OF THE STANDARD.—The international standard at present recommended shall be regarded as provisional for the next two years, in the hope that a more stable crystalline substance may in the meantime become available.

(*g*) SUBJECTS RECOMMENDED FOR FURTHER INVESTIGATION.—1. The influence of various oils as solvents upon the stability of solutions of irradiated ergosterol.

2. The crystalline antirachitic substances recently isolated from irradiated ergosterol. It was decided that Professor Windaus and Dr. Bourdillon shall be asked to investigate the constancy of the physical properties of the crystalline products recently isolated by them, respectively, in order to determine whether these may be regarded as pure substances. If so, the potency of these products should be accurately compared with that of the (present) international standard at intervals of three months during the next two years, in order to compare the stability in each case. If the results are satisfactory, it is hoped that one of these crystalline substances may eventually replace the solution of irradiated ergosterol as international vitamin *D* standard.

3. The toxicity of the present standard and of the crystalline products (see also Appendix, page 75).

(*h*) BIOLOGICAL METHODS FOR ESTIMATION OF VITAMIN *D*.—In using the international standard solution for the determination of the antirachitic potency of unknown preparations, it is recommended that not fewer than twenty rats (preferably more) be used for a determination, half of these to receive the standard and the remaining litter-mates the unknown substance. Provided this precaution is observed, it is considered permissible to use various biological methods of estimation, either prophylactic or therapeutic. For instance, the "line" test, *X*-ray examination, and determination of the bone ash, are all considered reliable methods.

III. THE ANTINEURITIC VITAMIN *B*

(*a*) INTERNATIONAL STANDARD.—*The Conference recommends the adoption, as international standard, of the adsorption product of the antineuritic vitamin* B *prepared in the Medical Laboratory, Batavia (Java), by the method of Seidell, as described by Jansen and Donath.*

(*b*) TERMINOLOGY.—The international standard preparation should be known as the "standard adsorption product of the antineuritic vitamin *B*."

(*c*) METHOD OF PREPARATION.—The international standard is prepared by extracting rice polishings with water, sufficient sulphuric acid being added to make the *p*H 4·5. Salicylic acid, to a concentration of 0·2 per cent., and toluene are then added to prevent bacterial decomposition. The process of extraction is continued for two days, after which the solution is filtered. For each 100 kilogrammes of the original rice polishings, 3 kilos. of fuller's earth (specially selected for its adsorptive powers) are added to the solution, which is then stirred for twenty-four hours. Subsequently, the solution is filtered off and the fuller's earth, after being washed with water and alcohol, is dried; 3 kilos. of the fuller's earth adsorbate represent the antineuritic vitamin *B* from 100 kilos. of rice polishings.

(*d*) PLACE OF PREPARATION.—It is recommended that the Medical Laboratory, Batavia, Java, should be asked, through Professor Jansen, of Amsterdam, to prepare a batch of 25 kilos. of the standard preparation. This should provide an adequate supply for many years.

(*e*) PLACE OF DISTRIBUTION.—It is suggested that this batch of standard adsorption product of antineuritic vitamin *B* should be kept at the National Institute for Medical Research, London, *acting for this purpose as central laboratory on behalf of the Health Organisation of the League of Nations.*

One hundred grms. would be an amount suitable for distribution to individual laboratories. No special precautions are necessary in keeping this preparation, except that it should be stored in a dry place. In the presence of moisture, bacterial decomposition readily takes place.

(*f*) Definition of Unit.—The unit recommended for adoption is the antineuritic activity of 10 mgrms. of the international standard adsorption product.

Note.—A daily dose of 10 to 20 mgrms. of this preparation is required to maintain normal growth in a young rat on a diet deficient in the antineuritic vitamin *B*, but complete in all other respects, including the antidermatitis vitamin (B_2); the curative "day dose" for a pigeon (300 grms. weight) suffering from polyneuritis on a diet of polished rice is about 20 to 30 mgrms. (method of Kinnersley and Peters).

(*g*) Permanence of the International Standard Recommended.—This standard adsorption product should serve as a provisional international standard for five years, or until advances in the knowledge of this vitamin make a revision desirable.

(*h*) Recommendations for Further Investigations.—1. The standard adsorption product should be investigated for its content of other vitamins *B*.

2. Although there is no evidence that loss of potency is liable to occur in the standard adsorption product, the Conference suggests that the following laboratories be asked to undertake a further investigation of its stability:

Department of Physiological Chemistry, University of Amsterdam.
National Institute of Health, United States Public Health Service, Washington, D.C.
Institute of Hygiene, University of Copenhagen.
School of Biochemistry, University of Oxford.
"Tierphysiologisches Institut," Leipzig.
Biochemical Institute, University of Stockholm.
"Laboratoire de physiologie au Centre de recherches sur l'alimentation (Institut des recherches agronomiques)," Paris.
Lister Institute for Preventive Medicine, London.

(*i*) Biological Methods for Estimation of the Antineuritic Vitamin *B*.—The Conference expresses no opinion on the relative merits of current biological methods for estimation of the antineuritic vitamin *B* (as recorded in the report on this vitamin, presented to this Conference and in the literature generally). It considers that good evidence is provided by that report that the different methods described, either prophylactic or curative in type, and employing either the rat or the pigeon as experimental animal, may yield equally valid results.

IV. THE ANTISCORBUTIC VITAMIN *C*

(*a*) International Standard.—*The Conference recommends the adoption as international standard of the fresh juice of the lemon,* Citrus limonum.

(*b*) Definition of Unit.—The unit of the antiscorbutic vitamin *C* recommended for adoption is the vitamin *C* activity of 0·1 c.c. of fresh juice of the lemon, *Citrus limonum.*

Note.—This is about 1/10th of the daily dose necessary to prevent development of macroscopic scorbutic lesions in a young guinea-pig maintained on a scurvy-producing diet.

(*c*) Method of Use.—The fresh lemon juice used as standard may be decitrated as follows: to the expressed juice, after filtration through muslin, an excess of calcium carbonate is added until effervescence stops. After standing for one hour, the mixture is filtered through a Buchner funnel. The decitrated juice should have a reaction of *p*H about 6 and should be administered to the experimental animal within two hours after filtration.

(*d*) Permanence of Standard.—This international standard shall be regarded as provisional for the next two years.

NOTE ON THE TOXICITY OF IRRADIATED ERGOSTEROL

In view of the toxic effects which have been reported after administration of certain specimens of irradiated ergosterol, this Conference suggests the advisability of testing all preparations of irradiated ergosterol, destined for medicinal use, for toxicity as well as for antirachitic potency.

APPENDIX

Memorandum on Carotene supplied for Testing its Suitability as a possible Standard for Vitamin *A*

Preparation.—The material provided has been prepared as follows:—Commercial carotene (B.D.H.) was dissolved in benzene and filtered, and the clear solution was poured into a large volume of warm absolute alcohol. The crystallisation was allowed to proceed at 37° C., and the crystals were filtered off at the same temperature. All these operations were carried out in an atmosphere of carbon dioxide. The crystalline material was dried *in vacuo*. Melting point 179° to 180° C. (taken in electrically heated "Berl block").

For distribution into tubes the material was dissolved in benzene at 37° C. to make a 2 per cent. solution; 0·5 c.c. of this solution was run into each of the brown glass tubes in which the material is distributed, the whole process of solution and filling out being again carried out in an atmosphere of carbon dioxide. The filled tubes were transferred to a desiccator containing paraffin shavings and calcium chloride. The desiccator was evacuated and left attached to the pump until the benzene had completely evaporated, and the carotene had been deposited, mainly as a crystalline residue, at the bottom of each tube. When drying was complete, the desiccator and contained tubes were again filled with carbon dioxide, evacuated, and refilled with carbon dioxide. The tubes, before filling, had been drawn out into narrow constrictions to facilitate sealing, which was thus rapidly effected with minimal contamination of the carbon dioxide by air.

Suggestions for Use.—It is assumed that less than the whole contents of one tube (10 mgrms.) will be required for a test. The tube having been opened, the necessary quantity of carotene can be removed with the aid of a fine glass rod or narrow platinum spatula, and immediately dissolved in the chosen solvent. The partly used tube should be enclosed in a test tube of suitable size, which should then be drawn out in preparation for sealing. The test tube and contained specimen tube can then be refilled with carbon dioxide in the vacuum desiccator, as above described, removed, quickly sealed, and preserved in a cold, dark place until again required. The prepared solution, if it is to be used for several tests, should be preserved from light and oxygen by similar or equivalent precautions.

Department of Biological Standards,
National Institute for Medical Research, London.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Detection of (1) Rye Flour in Wheat Flour and (2) Barley Flour in Rye and Wheat Flours. P. Rudolph and H. Barsch. (*Chem. Ztg.*, 1931, 55, 995–996.)—Rye and wheat flours may be distinguished from one another by stirring about 5 grms. of the material with sufficient hydrochloric acid (sp. gr. 1·124) to make a tough, pasty mass. When treated thus, rye meal soon assumes a red colour, which gradually increases in depth, whereas wheat flour exhibits no change. The presence of 10 per cent. of rye flour in wheat flour is detectable in this way.

The presence of barley meal in rye or wheat flour may be recognised as follows: 5 grms. of the flour are digested, with frequent swirling, with 50 c.c. of cold water. The mixture is filtered bright through a moist paper, and 10 c.c. of the filtrate are treated with 2 c.c. of hydrochloric acid (sp. gr. 1·124), which gives a pronounced turbidity and, on heating, a flocculent precipitate with either rye or wheat flour extract; with barley meal, no turbidity and, at most, a slight film is produced. Five c.c. of the acid wheat or rye extract, after cooling and filtering, or of the unfiltered acid barley meal extract, are treated with 10 c.c. of 96 per cent. alcohol. The barley extract immediately turns turbid, and, later, gives a flocculent deposit, whilst rye or wheat extract develops, at most, a very slight opalescence. An addition of 20 per cent. of barley meal to rye or wheat flour is readily detectable in this way.

Further, aqueous barley meal extract is coloured intensely yellow by 25 per cent. ammonia solution. Barley meal itself is coloured brown by 25 per cent. ammonia solution, whereas wheat flour is not changed in colour, and rye meal is turned a greenish yellow-grey colour. The oxygen of the air seems to play a part in the colour-formation, as the colour gradually increases in depth on the exposed surface of the flour. If the flours are stirred with ethyl acetate, instead of ammonia solution, barley meal becomes brown or brownish-yellow, and wheat or rye flour pale green. T. H. P.

Normal Proportion of Bromine in Edible Seeds, Wheat, and Bread. A. Damiens and S. Blaignan. (*Compt. rend.*, 1931, 193, 1460–1462.)—In order to determine whether bromine is normally present in plants, as it has already been shown to be in animals, the proportions of bromine, and of chlorine, and the ratio 1000 Br/Cl have been found for a number of samples of various cereal grains, beans, peas, bread, etc., and in every case, with the exception of rice and haricot beans, bromine was present. Wheat grains (3 samples) and bread (31 samples) contained, respectively, 0·21 and 0·09 to 0·61 mgrm. of bromine per 100 grms. of dry matter, and 0·07 and 0·82 to 1·8 of chlorine, the ratio 1000 Br/Cl being 2·8 and 0·07 to 0·46. The 1000 Br/Cl ratio for brewers' yeast was relatively high (5·2). Most of the other products examined showed a higher ratio than wheat, attaining 85 for lentils. D. G. H.

Indican in the Milk of the Cow and Goat. C. Hervieux. (*Compt. rend.*, 1931, 193, 1480–1482.)—A modification of Jolles' reaction for urine (*C.R. Soc. Biol.*, 1907, 63, 469) was used to detect indican in milk. One hundred c.c. of milk and 100 c.c. of dilute (1:5) trichloroacetic acid are mixed, and, after standing, 100 c.c. of the clear filtrate are collected. To this are added 10 c.c. of a 5 per cent. alcoholic solution of thymol, and to the cloudy liquid an equal volume of fuming hydrochloric acid containing 5 grms. of ferric chloride per litre. After standing for 1 hour, 10 drops of chloroform are added, and the mixture is shaken cautiously from time to time to get rid of emulsions. The chloroform gradually assumes the mauve or violet tint characteristic of indican in milk. Twenty-five individual and mixed samples of normal cow's and goat's milk were thus examined, and in every case the coloration was shown, and it is assumed that potassium indoxyl sulphate passes into the milk from the blood stream in the mammary glands. D. G. H.

New "Sorbite Process" for the Detection of Fruit Wine in Grape Wine. F. M. Litterscheid. (*Z. Unters. Lebensm.*, 1931, 62, 653–657.)—The wine is pre-treated according to Werder's method (ANALYST, 1929, 54, 476), and 100 c.c. of the decolorised liquid are evaporated on the water-bath to 4 to 5 c.c., and, after cooling for 10 minutes, the liquid portion is separated from the tartar by filtration through a plug of glass-wool into a 25 c.c., graduated, glass-stoppered cylinder. The residue is washed 5 times with 5 drops of water, and the total filtrate (not more than 6 c.c.) is shaken with twice the volume of hydrochloric acid (sp. gr. 1·18 to 1·19) and 0·2 c.c. of *o*-chlorobenzaldehyde for 1 minute, and then at intervals over 30 minutes. After 7 hours, the condensation-product of sorbitol and the reagent, which separates in voluminous white flocks, is removed by filtration (but not washed), and the filtrate is shaken with 5 drops more of reagent, any further precipitate being collected, after 5 hours, on the same filter. The combined precipitates are then washed with 50 to 60 c.c. of cold water, followed by 50 to

75 c.c. of cold methyl alcohol, the washings being collected separately from the filtrate, and the last traces being removed with the aid of a suction pump. Finally, the compound is dried for 30 minutes at 105° C.; it is readily soluble in chloroform and sparingly soluble in hot alcohol, and may be further purified (though this is not usually necessary) by precipitation with alcohol from a hot solution in chloroform, followed by crystallisation; it melts indefinitely at 175° to 210° C. (usually at about 200° C.). The filtrate from the second precipitation (excluding washings) is treated again with reagent, and any corresponding mannitol compound (m.pt. above 260° C.) will thus be obtained after prolonged standing. The sorbitol derivative is decomposed into its components by the action of 2 c.c. of warm hydrochloric acid (sp. gr. 1·18 to 1·19) per 1 grm. for 15 minutes, the excess of acid, together with the regenerated reagent, being expelled on the water-bath. The residue is then converted into hexa-acetyl sorbitol by the Lutin-Zăch method, in which it is warmed with 1 drop of pyridine and 1 c.c. of acetic anhydride (b.pt. 137° C.) per 0·1 grm. for 1 hour on the water-bath, the solution then being poured into hot water (2 c.c. per 0·1 grm.). Methyl alcohol is added to the mixture until there is no further disappearance of the solid on shaking, the solution is filtered while hot, and the acetyl derivative is allowed to crystallise (for 12 hours for small amounts). Satisfactory results were obtained for 0·1 per cent. solutions of mannitol or sorbitol, and for 2·5 to 10 per cent. by volume of decolorised apple wine in genuine white wine. J. G.

Detection of Cocaine in the Presence of Novocaine by means of Cobalt Thiocyanate. J. L. Young. (*Amer. J. Pharm.*, 1931, **103**, 709–710.)—Since the blue precipitate formed by the interaction of cobalt thiocyanate and the hydrochlorides of cocaine and novocaine is only soluble in a solution of stannous chloride in the case of novocaine, the two substances may be detected when present in combination. A few drops (4 to 5) of a 2 per cent. solution of cobalt thiocyanate are added to a small quantity of the salt under examination. If cocaine only is present, flakes of a Prussian-blue colour will form, whereas, with novocaine, or a mixture of novocaine and cocaine, the entire solution will become blue. On addition of 4 to 5 drops of freshly-prepared stannous chloride solution (5 grms. of tin added to 10 grms. of stannous chloride in 100 c.c. of 1:1 hydrochloric acid), the novocaine precipitate dissolves on stirring, leaving a pink solution; no change is apparent if only cocaine is present, and with both novocaine and cocaine, the precipitate of the former dissolves and the blue flakes or streaks of cocaine remain. D. G. H.

Quantitative Colorimetric Determination of *Digitalis* Glucosides by means of Baljet's Reagent. J. A. C. Van Pinxteren. (*Pharm. Weekblad*, 1932, **69**, 4–8.)—Baljet's colorimetric method (*id.*, 1918, **55**, 602) and modifications of the method proposed by Knudson and Dresbach (ANALYST, 1931, **56**, 675) are criticised. In particular, in the latter case it is difficult to match the digitalis picrate with potassium dichromate, as the solutions do not follow Beer's Law, and the intensity of the former colour doubles itself between 30 minutes and 2 hours after it is generated. Ouabain gives better results as a comparison colour standard, especially if 0·5 mgrm. of ouabain is added to the unknown solution before production of the colour, and due allowance is made for its presence in calculating the result. A Focke physiological value of 4 for Digitalis leaves was found to be equivalent to 1·7 mgrms. of ouabain per 50 mgrms. of leaf. A table of data relating the cat-physiological value (limiting dose per kilo.) and the ouabain value is given, but calculation of the former from the latter, based on an experimentally-found relationship for one sample of *Liquor digitalis* (cat-value 2 c.c. ≡ 0·78 mgrm. of ouabain) gives results in poor agreement with those found experimentally for other samples. The colorimetric value represents the resultant of those values due to all the glucosides present, *viz.* in an infusion, digitoxin 12·4, gitalin 72·2, and digitalin 15·4 per cent. (Hoekstra, *Diss. Utrecht*, 1931, p. 67). Colorimetric methods, therefore, cannot replace physiological methods with complete success. J. G.

Distribution of Saponin in *Agrostemma Githago* and in *Saponaria Officinalis*. F. G. de Wilde. (*Pharm. Weekblad*, 1932, 69, 65–78.)—*Determination of Saponin.*—A physiological method is considered preferable to chemical methods (*cf.* Kofler, ANALYST, 1922, 47, 403; 1924, 49, 239). A 1:50 to 1:400 decoction of the powdered drug is prepared (according to *Ned. Pharm.*, Ed. V) in a physiological salt solution adjusted to *p*H 7·4 with a phosphate buffer, and is filtered when cool, and 0·95, 0·90, 0·85, etc., down to 0·50 c.c., are diluted in separate test-tubes to 1 c.c. with the buffered saline. Each solution is then shaken with 1 c.c. of a 4 per cent. suspension of washed blood corpuscles in buffered saline, and, after 12 to 20 hours, the haemolytic index is given by the greatest dilution of drug producing complete haemolysis. A parallel experiment with "Saponin pur. albiss. Merck" (index 25,000) under the same conditions, provides a quantitative means of standardisation. *Determination of Sugars* (*cf.* MacLean, *id.*, 1919, 44, 344).—A decoction of 1 grm. in 50 c.c. of water is prepared by the official method and, after replacement of any water lost by evaporation, 40 c.c. of the cool, filtered solution are treated with basic lead acetate solution until no further precipitate results, when the mixture is diluted to 50 c.c. and filtered. Excess of lead is removed by addition of excess of sodium sulphate solution to 40 c.c. of the filtrate, which are then diluted to 50 c.c., filtered again, 1 to 5 c.c. being diluted to 20 c.c. with a solution containing 15 grms. of sodium sulphate and 0·1 c.c. of acetic acid per 100 c.c.; 2 c.c. of a solution of 12 grms. of potassium hydrogen carbonate, 8 grms. of potassium carbonate, 0·350 grm. of copper sulphate, 0·050 grm. of potassium iodate and 0·500 grm. of potassium iodide (presumably in 50 c.c., *cf. loc. cit.*) are then added. The mixture is heated to boiling in 1 minute 40 seconds, and, after a further 6 minutes, it is cooled and the iodine liberated by addition of 2 c.c. of 25 per cent. sulphuric acid is titrated after 1 minute with 0·0025 *N* sodium thiosulphate solution in the presence of 3 drops of a 1 per cent. solution of starch. Allowance is made for the blank on the reagents, and a table is given relating the titration to the dextrose value. For an inversion, 10 c.c. of cleared decoction are heated with 1 c.c. of 25 per cent. hydrochloric acid for 5 minutes at 70° C., and the cooled solution is neutralised to methyl red, and then diluted to 20 to 40 c.c., and treated as described.

Distribution of Saponins and Sugars during the First Year of Growth of Agrostemma Githago.—Three periods were studied, *viz.* (1) the appearance of the first stem leaves; (2) growing period; (3) ripening period. No data are given, but, in general, an increase in saponin, especially during the early stages of germination of the seed, corresponding with a decrease in sugar, was observed. It is suggested, therefore, that the saponin results as an intermediate product in the breakdown of more complicated reserve material, and can itself serve as a reserve material. Analyses of other parts of the plant confirm this theory. The total saponin content of the bud is the same as that of the flower after complete development, but decreases when fading sets in.

Saponaria Officinalis gave results in confirmation of the theory, though these are somewhat complicated by the fact that the plant was over a year old. J. G.

Denicotinisation of Tobacco Smoke during Smoking. R. Kissling. (*Chem. Ztg.*, 1932, **56**, 31.)—Methods hitherto employed for removing nicotine have usually involved the passage of the smoke through an asbestos wad impregnated with gallotannin or ferric chloride, but have seldom proved very effective. "Bonicot's fluid," 3 drops of which are placed in the "head" of the cigar, was found to contain 96·60 per cent. of water, 2·73 per cent. of alcohol, and 0·67 per cent. of solids (mainly ferrous ammonium sulphate, with small amounts of citric and tartaric acids and traces of sodium chloride; *cf. Eng. Pat.*, 1931, 348,974). Trials were made with a number of varieties of Brazilian cigars (about 5 grms. in weight), smoked in batches of 10, at the rate of 30 minutes each, 24 per cent. of the original weight being left unsmoked. The original nicotine content was about 1 grm. per 10 cigars, of which 0·240, 0·233 and 0·197 grm. were found in the unsmoked ends, and 0·450, 0·480 and 0·493 grm. in the smoke, in experiments with Bonicot's liquid, distilled water and untreated cigars, respectively. Bonicot's liquid, therefore, has relatively little effect. J. G.

Determination of Phenol and its Homologues in Disinfecting Fluids. A. F. McCarley. (*J. Soc. Chem. Ind.*, 1932, **51**, 38T.)—Phenol may be satisfactorily and conveniently determined in disinfecting fluids (containing up to 5 per cent. of phenols) by treating 50 grms. of the sample with 100 c.c. of saturated barium hydroxide solution and 25 c.c. of barium chloride in a 750 c.c.-flask immersed in boiling water for 15 minutes, with constant shaking. The liquid is filtered through a coarse paper on a fluted funnel, and the contents of the paper are scraped back into the flask, and treated as before with 50 c.c. of barium hydroxide solution and 20 c.c. of barium chloride solution. Vigorous shaking will cause an agglomeration, and the clear liquid can be readily filtered. The conglomerate is again treated with barium hydroxide. Any uncombined oil is removed from the combined filtrates by shaking with petroleum spirit, and the alkaline solution is treated with excess of hydrochloric acid. The acid solution is then extracted 3 times with methylated ether, and the ethereal solution is washed with sodium carbonate solution. Three extractions with sodium hydroxide solution are then made, and the alkaline solution is evaporated to 15 c.c. and treated with sulphuric acid in a burette. The volume, multiplied by 2·1, gives the percentage of phenols. Results were in agreement with those obtained by the method involving steam distillation and subsequent titration with soda. D. G. H.

Determination of the Total Nitrogen and Solid Matter in Yeast. R. S. W. Thorne. (*J. Inst. Brewing*, 1932, **38**, 23–29.)—Neither the original Kjeldahl method nor the Gunning modification thereof (with or without added potassium permanganate) determines the whole of the nitrogen in yeasts of all kinds, the results being low, sometimes to the extent of 10 per cent. Values corresponding with 99 to 100 per cent. of those furnished by the Dumas method are, however, obtained in all cases by the following modified procedure, suggested by Fulmer and Christensen (*J. Phys. Chem.*, 1925, **29**, 1415): A mixture of about 0·5 grm. of the yeast with 0·4 grm. of copper sulphate, 10 grms. of potassium sulphate, 1 c.c. of concentrated sulphuric acid, and 30 c.c. of 50-volume hydrogen peroxide solution (15 c.c. of 100-volume peroxide diluted to 30 c.c. with water) is evaporated slowly almost to dryness on a steam-bath; 20 c.c. of concentrated sulphuric acid are then added, and the digestion is continued in the usual way. The use of too great an excess of hydrogen peroxide causes low results, but the proportions stated above prove satisfactory, even when the strength of the peroxide solution employed has fallen to 90 per cent. of its original value.

With wort, also, the Kjeldahl-Gunning method yields low results, and determinations made by this method on a fermenting wort 0, 2, 3, 4, and 7 days after the commencement of fermentation, gave proportions of nitrogen lower by 1·5, 3·7, 5·5, 5·1, and 4·3 per cent., respectively, than those yielded by the Fulmer and Christensen method.

For the routine determination of the total solid matter in yeast, the following rapid method gives figures in almost exact agreement with those obtained by Fletcher's method (*J. Inst. Brewing*, 1931, **37**, 506), according to which the yeast is treated with a little absolute alcohol—to arrest enzyme action at once—and is then dried to constant weight in a steam-oven: The yeast (1 to 2 grms.) is weighed into a flat-bottomed nickel dish and moistened with a few drops of absolute alcohol. About 1 c.c. of water is then added, and the whole stirred into a paste. This is dried as completely as possible on a steam-bath (in about 5 minutes) and placed in a Mojonnier oven for 1 hour, after which time it will have reached constant weight. The object of making the yeast into a paste with water is to obtain a uniform layer at the bottom of the dish, and so to avoid discrepancies which might arise if the yeast were dried in irregular lumps. T. H. P.

Biochemical

Determination of the Iodine Value of Oils and Lipids. M. Yasuda. (*J. Biol. Chem.*, 1931, **94**, 401–409.)—A method published by Rosenmund and Kuhnhenn (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 154; ANALYST, 1924, **49**, 105) for the determination of the iodine value of fats and oils, in which pyridine sulphate dibromide was used as a halogenising agent, was used later for the micro-determination of the iodine value by Dam (*Biochem. Z.*, 1924, **152**, 101; 1930, **220**, 158) and by Page (*Biochem. Z.*, 1930, **223**, 445). A comparison was made between the Hanus method and the Rosenmund–Kuhnhenn method, with special reference to the time required for the reaction, and the amount of halogen used in the two methods. Determinations of the iodine value were made by both the Hanus and Rosenmund–Kuhnhenn methods on oleic, ricinoleic and linolic acids, cholesterol, cholesteryl palmitate and cod-liver oil. Ricinoleic acid was taken as an example of unsaturated hydroxy fatty acid; cod-liver oil served as an example of a mixture of various lipids. Tables and a figure show the results, from which the following conclusions are drawn:—(1) For the determination of the iodine value of oleic and ricinoleic acids the Hanus and the Rosenmund methods give the same value, which is very near the theoretical. (2) For linolic acid and cod-liver oil the Hanus method gives values 2 to 4 per cent. higher than the other. (3) With linolic acid the Rosenmund method is much less influenced by the amount of halogen than the Hanus method. (4) The Hanus method is not suitable for the determination of the iodine value of cholesterol and its esters; the values obtained by this method deviate greatly from the theoretical value. Therefore, the Rosenmund–Kuhnhenn method was applied to the determination of the iodine value of small amounts of various lipids in the tissues of the animal body; *i.e.* to the total fatty acids, phospholipid, and its fatty acids. The micro method, which is described, is simple and easily carried out, and was found to give exactly the same iodine values as the macro method for standard lipid solutions, namely, 90 for oleic, 85 for ricinoleic, and 160 for linolic acid. The excess of halogen should be at least 25 per cent. in the case of oleic acid, and about 260 per cent. in the case of linolic acid. Procedure is described by which the iodine value of lipids in small amounts of tissues can be determined by the use of the pyridine dibromide solution of Rosenmund and Kuhnhenn and the oxidative micro method for the determination of lipids of Bloor (*J. Biol. Chem.*, 1929, **82**, 273; 1928, **77**, 53). Some results obtained with rat tissues are given. P. H. P.

Determination of Galactose in Blood and Urine. V. J. Harding and G. A. Grant. (*J. Biol. Chem.*, 1931, **94**, 529–539.)—Knowledge of the metabolism of galactose is hampered by lack of a suitable analytical method. Ordinary bakers' yeast used in comparatively large quantities for a short time has proved a very useful reagent for the removal of glucose from biological fluids, such as blood and urine. Many yeasts have the power of fermenting galactose, especially if they are first grown on a nutrient medium of hydrolysed lactose, or on galactose itself (*i.e.* if they are acclimatised). Both Abderhalden (*Fermentforschung*, **1924**, **8**, **42**) and von Euler and Nilsson (*Z. physiol. Chem.*, 1925, **143**, 89) showed that galactose-acclimatised yeast could be dried and sterilised, and yet retain its power of fermenting galactose. There thus seemed no reason why such an acclimatised yeast should not be used as an analytical reagent for galactose, in a manner analogous to ordinary yeast for glucose. It would first be necessary to remove the ordinary fermentable sugars, and then to treat the fluid with the acclimatised yeast. Ordinary bakers' yeast was acclimatised to galactose for three 3-day incubation periods; the preparation obtained was called "galac" yeast. Under the analytical conditions described, galac yeast does not remove maltose, lactose, arabinose, xylose, or glutathione; it removes glucose, fructose, mannose and sucrose, as well as galactose. The method of determination takes a larger amount of yeast and a slightly longer time than the usual process for removing glucose, and attempts were made to reduce both these factors. For determinations of galactose in blood or urine the fermentable sugars are removed from a sample by means of ordinary yeast, the fermentable sugars, plus galactose, are removed from a second sample by means of galac yeast, and the difference represents galactose. The results show that ordinary bakers' yeast, grown in a medium containing galactose, can be utilised to remove galactose quantitatively from aqueous solutions, from Folin–Wu blood filtrates, and from urine treated with sulphuric acid and Lloyd's reagent. No galactose can be found in normal blood (either plasma or corpuscles) or in normal urine during fasting. No galactose can be found in blood after fasting or in urine, in late pregnancy or 3 days' *post partum* at the beginning of lactation. The non-fermentable "sugar" found in urine after fasting, in late pregnancy, and the *puerperium*, on hydrolysis, gives "fermentable sugar" and "galactose sugar." The amounts of "fermentable sugar" and "galactose sugar" on hydrolysis are inconsistent with the idea that lactosurias are produced by the simple addition of lactose to the normally occurring non-fermentable urinary reducing substances.

P. H. P.

Colorimetric Method for Determination of Allantoin. H. W. Larson. (*J. Biol. Chem.*, 1932, **94**, 727–738.)—The method of Wiechowski (*Beitr. chem. Physiol. u. Path.*, 1908, **11**, 109) for the determination of allantoin, as modified by Handovsky (*Z. physiol. Chem.*, 1914, **90**, 211), is the one now in general use. However, the published methods for allantoin determination occupy from 6 to 24 hours, and most of them are probably inaccurate, giving, at best, only approximate values. The need for a more accurate and rapid method has become urgent, owing to the importance of animal purine metabolism. Folin and Svedberg (*J. Biol. Chem.*, 1926, **70**, 418), in working with various copper reagents for carbohydrate determination, developed an ammoniacal copper reagent which is practically unaffected by urinary sugar, but which is reduced by nitrogenous compounds such as creatine, creatinine and allantoin. With the use of this reagent a rapid and accurate colorimetric method for the determination of allantoin has now been devised; the general outline of the method is as follows:—Five c.c. of animal urine are treated with an excess of 30 per cent. phosphotungstic acid, followed by an excess of saturated basic lead acetate solution and 5 per cent. sulphuric acid. This treatment removes interfering substances. The procedure is carried out in the same 50 c.c. centrifuge tube. After the addition of each reagent the tube is gently rotated to insure proper mixing, and the mixture is centrifuged until perfectly clear, when 2 c.c. of this liquid are pipetted into a Folin-Wu sugar tube together with 2 c.c. of Folin's ammoniacal copper reagent, which is reduced by allantoin. This tube is then heated in a boiling water-bath for 10 minutes, cooled, and 2 c.c. of acid molybdate reagent are added. The colour obtained is compared with an allantoin (1 mgrm.) standard. Recoveries of allantoin added to rat urine range from 90 to 100 per cent. Two hours are sufficient for the complete determination, whereas the Wiechowski–Handovsky method requires 10 or 12 hours. The method was designed primarily for use with rat urines, but has been used successfully with other urines. It depends upon a proper balancing of reagents involved. A table gives comparative allantoin values obtained by the Wiechowski–Handovsky method and by the colorimetric method.

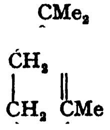
The colorimetric values differ from the others by −24·0 per cent. to +31·7 per cent. The Wiechowski–Handovsky method shows low recoveries of added allantoin. In general, the colorimetric method gave higher allantoin values than the Wiechowski method, and experiments were devised to prove that the reduction of the copper reagent came from allantoin only, and not from other substances which might be present. It is suggested that one source of error in the Wiechowski–Handovsky method is the considerable loss of allantoin due to adsorption on the bulky precipitates of lead and silver sulphides. By a modification of the colorimetric procedure 25 mgrms. of allantoin were obtained from 1205 c.c. of human urine excreted during 24 hours. Specimens of mixed human urines yielded 25 and 30 mgrms. of allantoin per litre. Mercury-allantoin precipitates were decomposed with hydrogen sulphide; after being recrystallised twice the allantoin obtained melted at 236–237° C. P. H. P.

Vitamin *A* from Fish Oils. II. P. Karrer, R. Morf and K. Schöpp. (*Helv. Chim. Acta*, 1931, 14, 1431–1436.)—In continuation of their work on *Hippoglossus hippoglossus* (ANALYST, 1931, 56, 824) the authors have found that high Lovibond (vitamin *A*) values are obtainable from the unsaponifiable matter of the oil from *Scombresox saurus* (mackerel species). Sterols were, therefore, frozen out from a solution in methyl alcohol by means of a mixture of carbon dioxide and acetone, and an extract in petroleum spirit of the residual solution (containing the vitamin *A*) was passed through a filter-column containing fibrous adsorbent alumina (*cf. loc. cit.*). The top layers were then found to contain traces of sterols, whilst the relatively low Lovibond values of the bottom layers indicated, probably, the presence of compounds of lower molecular weights. The middle portion, which gave the highest Lovibond value, was further purified by fractional adsorption twice on argillaceous earth, and each adsorbate was divided into 3 fractions, the middle fraction of which was dried in a vacuum and analysed ($C_{20}H_{30}O$ or $C_{22}H_{32}O$); a third adsorption produced no appreciable change in composition. The resulting compound had the properties of an alcohol capable of forming esters (*cf.* Vogt, *Merck's Jahresber.*, 1930, p. 34), which often differed in solubility from the original substance, notably in being soluble in cold methyl alcohol. This provides a means of separation and purification (by fractional solution 5 times) of the *p*-nitrobenzoic acid ester, which was shown to have the formula $C_{20}H_{29}O.CO.C_6H_4NO_2$. The acetic ester ($C_{20}H_{29}O.COCH_3$), which is produced by the action of acetic anhydride in pyridine solution, is also sparingly soluble in methyl alcohol, and may be saponified by an alcoholic alkaline solution at 60° C., and the vitamin substance thus regenerated may be shown to have the same composition and Lovibond value as the original. The vitamin compound (*cf. loc. cit.*) is a clear, pale-yellow viscous oil, fluid when warm; its optical inactivity indicates the absence of active sterols, whilst animal experiments confirm the absence of vitamin *D*. Geronic acid results from the action of ozone, and acetic acid is produced by decomposition with potassium permanganate or chromic acid, whilst catalytic reduction and distillation in a vacuum yield a compound having the formula $C_{20}H_{40}O$ or $C_{22}H_{44}O$. It appears to resemble carotene in structure, having a similar carbon ring (*vide infra*), and an aliphatic side-chain (on the C atom indicated), which is given by the authors as

$$-CH{=}CH-C(Me){=}CH-CH{=}CH-C(Me){=}CH-CH{=}CH-CH_2OH,$$

or $$-CH{=}CH-C(Me){=}CH-CH{=}CH-C(Me){=}CH-CH_2OH.$$

Its Lovibond value is not greater than that of the *Hippoglossus* product (*loc. cit.*), and further work on this point is in progress. J. G.



Assay of Antineuritic Vitamin and its Concentration with Silver. R. J. Block, G. R. Cowgill and B. H. Klotz. (*J. Biol. Chem.*, 1932, **94**, 765–782.)—The method of assay for antineuritic vitamin *B* used in the investigation is described. It is a combination of weight-maintenance and curative techniques carried out on pigeons given a diet of polished rice *ad libitum*, supplemented daily with meat residue, cod-liver oil, and the Osborne–Mendel salt mixture. The plan of assay differs from that of many other workers, in that polished rice does not constitute the *sole* diet. Since it is not a complete food, the polished rice, if it is to be used, should be supplemented, so as to supply a food mixture deficient only in respect of the one variable of interest, namely, antineuritic vitamin *B*. In this case the polished rice serves as the chief source of calories, the meat residue as a source of good protein and heat-stable vitamin $G(B_2)$ factor, relatively free from antineuritic vitamin, the Osborne–Mendel salt mixture furnishes the mineral nutrients, and the cod-liver oil supplies the fat-soluble vitamins. The supplements are given (in sufficient quantities to meet the requirements) in a gelatin capsule; one capsule is given daily to each bird. Ten experiments were carried out on the concentration of the antineuritic vitamin by means of silver. As sources of the silver ion, the nitrate and lactate were used; nitric, sulphuric or lactic acid was employed as source of the hydrogen ion; and barium or sodium hydroxide was used for alkalising (to bring the reaction from *p*H 4 to *p*H 7·0). Silver nitrate, lactic acid and barium hydroxide gave the most favourable purification with the least loss of activity; treatment with silver lactate, lactic acid and sodium hydroxide resulted in the greatest increase of potency, but in a poor yield of the vitamin. The behaviour of antineuritic vitamin in the ternary mixture of water, ethyl alcohol and carbon tetrachloride was studied. Whereas the inorganic salts are precipitated as the water is removed and the concentration of the alcohol approaches 100 per cent., it was found that the vitamin remains in the liquid phase, from which it may be recovered quantitatively. Solubility of the vitamin in other binary mixtures was studied. Six other alcohols were substituted for ethyl alcohol in the carbon tetrachloride procedure; of these, only *n*-butyl and allyl proved to be as good as ethyl alcohol for concentrating the vitamin. The solubility of the antineuritic vitamin in mixtures of methyl alcohol with acetone, allyl and amyl alcohols was studied. None of these mixtures can be used profitably to concentrate the vitamin. P. H. P.

Preparation of Vitamin *C* Concentrates from Lemon Juice. J. S. Svirbely and C. G. King. (*J. Biol. Chem.*, 1931, **94**, 483–490.)—In order to investigate the preparation of concentrated antiscorbutic fractions from lemon juice, a study was first made of the solubility of the active material in organic solvents. It has been shown that vitamin *C* is soluble in mixtures of petroleum spirit and acetone (1:1), petroleum spirit and butyl alcohol (2:1 and 4:1) and petroleum spirit and propyl alcohol (1:1 and 3:1) in ethyl acetate, butyl alcohol and propyl alcohol, but is insoluble in absolute ethyl ether. Ammonia gas destroys the active material when passed into solutions containing the vitamin dissolved in organic solvents. The general procedure used in testing the vitamin *C* content of the various fractions was that recommended by Sherman, La Mer and Campbell (*J. Amer. Chem. Soc.*, 1922, **44**, 165; ANALYST, 1922, **47**, 216), with shorter test periods. Details have been worked out for the preparation of active fractions from volumes of lemon juice up to 2·5 litres. The method is approximately the same as that previously reported by Grettie and King (*J. Biol. Chem.*, 1929, **84**, 771), and by Sipple and King (*J. Amer. Chem. Soc.*, 1930, **52**, 420), with certain modifications and precautions found necessary when dealing with larger quantities of juice. The most concentrated preparations yet obtained (0·03 to 0·5 mgrm. of total solids per c.c. of lemon juice) are sufficiently stable to be kept for weekly feeding periods, and have given no indication of more than one factor being involved. Evidence was given previously by McKinnis and King (*J. Biol. Chem.*, 1930, **87**, 615; ANALYST, 1930, **55**, 592) that vitamin *C* is probably acidic in nature. In the present investigation the active material obtained was consistently characterised by being distinctly acidic, and exerted a strong reducing action. Tests for carbylamine and phenols were negative. Strongly positive tests were obtained with orcinol (blue-green) and resorcinol (pink). P. H. P.

Chemical Investigations on the Antiscorbutic Vitamin. I. O. Rygh, A. Rygh and P. Laland. (*Z. physiol. Chem.*, 1932, **204**, 105–111.)—Previous chemical investigations on vitamin *C* are outlined (*cf.* Zilva, ANALYST, 1927, **52**, 425, 552; 1928, **53**, 552; 1930, **55**, 289; Veeder and Lawson, *id.*, 1927, **52**, 424), and the resulting conclusions regarding the chemical properties of the pure vitamin are used as a basis of isolation. *Isolation.*—Freshly-pressed apple juice or lemon juice was evaporated to one-fifth of its volume under reduced pressure (below 25° C.), and oils and phytosterols were removed by extraction several times with ether (free from peroxides). The solution was then neutralised to litmus and was again extracted repeatedly with an equal volume of ether, the extract being dried by means of sodium sulphate and distilled. These operations were carried out, as far as possible, in an atmosphere of carbon dioxide or nitrogen. In some cases hydrogen chloride gas was bubbled into the concentrated ethereal solution and the resulting precipitate was collected. The yields were 600 and 50 mgrms. from 10 litres of unripe orange juice and 40 litres of apple juice, respectively (*cf.* following abstracts). In all cases mixtures containing variable proportions of crystals and a heavy oil were obtained which, on recrystallisation from alcohol, gave needles only, m.pt. 172° C. (176° C. after further treatment with animal charcoal). Their physical properties (including solubility, mixed m.pt., ultra-violet spectrum, $[\alpha]_D$), molecular weight (determined by titration with alkali of a solution in acid), and chemical tests (Mayer's reagent, the sodium acetate and sulphuric acid tests, elementary analysis, salt formation) showed them to be identical with narcotine. Pure narcotine, however, has no antiscorbutic properties, but experiments with 15,000 apples of various degrees of ripeness showed that the narcotine content increases with the degree of ripening, a negligible amount being found in the fully-ripe fruit. These, and experiments on animals, indicate that narcotine is the precursor of vitamin *C*, which is formed from it during the ripening process.

Animal and Irradiation Experiments.—Batches of six guinea-pigs were fed on a basic diet containing 340 grms. of casein, 1280 grms. of maize starch, 40 grms. of physiological salt mixture, 30 grms. of sodium chloride, 100 grms. of calcium lactate and 50 grms. of filter paper, which were cooked with 3 litres of water, and the resulting pulp was mixed with 200 grms. of yeast extract, 125 grms. of butter, and 10 c.c. of cod-liver oil. A Uviol tube containing 2 grms. of commercial narcotine and 25 grms. of ethyl acetate was exhausted at a pressure of 2 mm. and sealed, and was then exposed for 2 hours at 25 cm. from a mercury lamp. The temperature rose to 40° C., and the narcotine dissolved, but was deposited on cooling, and was then recrystallised from alcohol, yielding pale yellow needles, m.pt. 172° C. Fivefold recrystallisation produced no change in m.pt., but treatment with animal charcoal raised it to 176° C. Further irradiation produced a brown resinous mass which was insoluble in acids and in the ordinary solvents; $[\alpha]_D$ was unchanged. All guinea-pigs fed on the above diets, with or without addition of 0·5 mgrm. per day of ordinary or irradiated narcotine dissolved in dilute tartaric acid solution, died after 4 to 5 weeks, showing symptoms of scurvy, except in the last instance. These experiments are being continued (*cf.* Bezssonoff, *Bull. Soc. Chim. Biol.*, 1927, **9**, 555; Zilva, *Biochem. J.*, 1924, **18**, 632, 641; 1927, **21**, 354; 1928, **22**, 779). J. G.

Experiments on the Isolation of Narcotine from Different Vegetables and from Milk. P. Laland. (*Z. physiol. Chem.*, 1932, **204**, 112–114.)—Narcotine was isolated from the undermentioned young, unripe vegetables by appropriate modifications of the method already described (*cf.* preceding abstract), the mixture of oil and crystals being then extracted in dilute tartaric acid, the former separated and the latter precipitated with sodium hydroxide solution and extracted with ether. The final product was dried in a vacuum at 60° C., and was then obtained as needles (m.pt. 172° C.), which, after treatment with animal charcoal, melted at 176° C., and had all the properties of narcotine (*cf. loc. cit.*). *Tomatoes.*—Twenty kilos. yielded a juice of *p*H 4·2 and 20 mgrms. of narcotine. *Cabbages.*—One hundred kilos. yielded 25 litres of juice; *p*H, 6·3, yield 40 mgrms. *Potatoes.*—Twenty kilos. yielded 10·4 kilogrms. of juice; *p*H, 5·6, yield 12 mgrms. *Mountain cranberries.*—Seventy-five kilos. taken; juice weakly antiscorbutic; *p*H 2·87; yield none. *Milk.*—The casein was precipitated by acid from 50 litres and the filtrate was treated as described; the yield was very small (*cf.* following abstract). J. G.

Chemical Investigations on the Antiscorbutic Vitamin. II. Narcotine and its Derivatives as Antiscorbutics. O. Rygh and A. Rygh. (*Z. physiol. Chem.*, 1932, **204**, 114–122.)—Guinea-pigs were fed on a basic diet containing oats-grits 50 parts, wheat bran 20, skim-milk powder (autoclaved for 2 hours at 110° C.) 15, fresh butter containing 1 per cent. of cod-liver oil 10, common salt 1, and Osborne's physiological salt mixture 0·5 part, to which was added a solution in dilute tartaric acid of the substance to be tested. The animals, including the controls, were killed after 30 days and dissected, and 0 to 10 points were allotted according to the degree of scorbutic attack observed in the various parts of the body (*i.e.* 10 corresponds with the highest degree of attack), a final value being obtained from the mean of the observations for the individual organs. Irradiated narcotine (*cf.* preceding abstracts) gave values as follows:—A daily dose of 10 mgrms., 4; 5 mgrms., 2; 2 mgrms. to 100γ, 0; 10 to 1γ, 5 to 6; 0·1γ, 7; control, 9. The intestine and suprarenal showed no scorbutic effect for doses of 10 mgrms. to 10γ, and no *X*-ray evidence of scurvy was obtained for 2 mgrms. to 100γ (*i.e.* 0 points). The leg-bone and rib values fell to 0 at 1 mgrm., and at 2 mgrms. to 100γ, respectively, and then increased. Antiscorbutic value was absent from cotarnine, meconine, cotarnaminic acid and normeconine, and feeble in anhydrocotarnine phthalide and narcotine-*n*-oxide; dimethyl nornarcotine, nornarcotine, and especially, methyl nornarcotine were active, and the last was selected for further tests. It is an *o*-dihydroxy derivative obtained after removal of the 2 methyl groups from the pair of adjacent methoxy groups in the narcotine by heating it for 8 days at 100° C. with an 8-fold volume of concentrated hydrochloric acid, followed by recrystallisation and treatment with hydriodic acid. Its hydrochloride is red, but it is bleached by sulphur dioxide, though not by animal charcoal, and it is soluble in dilute alcohol or in water to give a frothy solution, which gives a precipitate with acids if the solution is concentrated. It gives a positive phenol reaction and has strong reducing properties, being readily oxidised to a brown substance (*cf.* Matthiessen, Foster and Wright, *Proc. Roy. Soc.*, 1860 to 1870). *Animal experiments.*—Five mgrms. to 100γ, 3 to 1; 100γ to 10γ, 0; 1γ, 4; 0·1γ, 6; control, 9 to 10. Thus, a dose of 20γ gave the optimum antiscorbutic value (*i.e.* lowest average of points). The suprarenal and intestine were unaffected throughout. It is stated that the action of germinating seeds also converts narcotine into an antiscorbutic substance having the reactions of a phenol. The relation of these data to the effects of other vitamins and of other constituents of the basic diet is discussed (*cf.* Rygh, Rygh and Laland, preceding abstracts, and *Z. physiol. Chem.*, 1931, **200**, 261).* J. G.

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* S. Smith and S. S. Zilva, at a meeting of the Biochemical Society (*Chem. and Ind.*, 1932, **51**, 166), described experiments which do not confirm the conclusions of O. and A. Rygh.—EDITOR.

Bacteriological

Distribution of Agar-liquefying Bacteria. H. Nicol. (*Nature*, 1931, **128**, 1041–1042.)—Several strains of an organism which attacks and softens agar-agar have been isolated from a swampy garden soil from Palmer's Green and from the clover side of Agdell Field, Rothamsted, both sampled in wet weather in spring. The organisms form small, slowly-growing, yellow colonies, which develop well in the usual agar media, and are invariably situated in the centres of circular areas of softening. A characteristic "hammered copper" appearance is thus given to the plate. No strain liquefies the agar, but, in stroke cultures, the whole of the agar is, in time, softened, although growth proceeds only on the surface. Optimum growth occurs mostly in a medium containing about 0·3 per cent. of sodium chloride, but one strain (Palmer's Green) grows on a medium similar to Gran's, with 3 per cent. of salt. The presence of dextrose depresses the development of most of the strains. The organisms were isolated from filter-paper strips during a search for cellulose-decomposing bacteria, with which the agar-liquefiers are frequently associated. T. H. P.

Effect of Rhizopin on the Growth of Aspergillus Niger. N. Nielsen. (*Compt. rend. Lab. Carlsberg*, 1931, 19, No. 5, 1–10.)—It was shown earlier that growth of *Rhizopus suinus* under certain special conditions is accompanied by the separation of a substance, termed rhizopin, which is able to promote the development of the *Avena coleoptiles*. It was found, also, that rhizopin solutions further the growth of yeast, but whether the same substance is the active component in the two cases remains undecided. Further work shows that rhizopin solutions increase the growth of *Aspergillus niger* to as much as nine times the normal yield, and also enhance conidia-formation by this organism. T. H. P.

Organic Analysis

Industrial Analysis of Glacial Acetic Acid. E. Charles. (*Ann. Chim. anal.*, 1932, 14, 5–13.)—The formic acid, water, and higher acids present in glacial acetic acid may be determined by the following procedure: (1) The melting-point of the acid is measured, conveniently in a test-tube with a 15 c.c. bulb blown at the bottom. About three-fourths of the bulb is filled with the acid, into which a thermometer, reading to 0·05° C., and allowing the temperature to be estimated to within 0·02° C., is dipped. The tube is cooled in either ice-water or a mixture of crystalline sodium sulphate and hydrochloric acid, the acid being stirred with the thermometer. When solidification occurs—usually at a temperature about 10° C. below the melting point—the tube is transferred to water at 20° C. and stirred. When only a small quantity of crystals remains, the tube is withdrawn from the water and the first reading of the temperature is made. The tube is then placed again in the cooling mixture and the operations are repeated until a concordant melting point (A_1) is obtained. The difference of this value from 16·70° C. is due to the various impurities.

(2) The formic acid may be determined in various ways: (*a*) In conjunction with the water, by measuring the carbon monoxide evolved during the reaction with acetic anhydride; a special apparatus for this is described. (*b*) By Daniel's method (ANALYST, 1927, 52, 549). (*c*) By utilising the reaction with bromine, $H.CO_2H + Br_2 = 2HBr + CO_2$; use is made of aqueous bromine solution saturated at 18° to 20° C., this containing 31·5 grms. of bromine per litre (≡9 grms. of formic acid). Ten c.c. (or about 10·5 grms.) of the acid are shaken with 25 c.c. of 20 per cent. sodium carbonate solution to expel the carbon dioxide, and the bromine water is then run in from a burette until a yellow coloration persists for some minutes. The volume V of bromine solution used is diminished by 0·35 c.c., this

quantity in excess being required to give the coloration. The percentage F of formic acid is given by $F = 0{\cdot}086\ (V - 0{\cdot}35)$.

(3) A rapid determination of the water may be made as follows: 95 c.c. (100 grms.) of the acid, 3 drops (0·1 grm.) of sulphuric acid (66° Bé.) and 5 c.c. of acetic anhydride of known titre (to obtain more exact results, the materials should be weighed) are boiled together gently for 5 minutes in a 200 c.c. flask fitted with an air-cooled reflux tube. The flask is then cooled and the melting point of the contents measured; this temperature, increased by 0·04° C. (lowering due to the sulphuric acid), gives A_2. If the subsequent calculation shows that all the acetic anhydride taken has reacted, the test must be repeated with a greater amount of the anhydride; for great accuracy, the excess of the anhydride over the amount which reacts with the water and with the formic acid should be as small as possible. All reagents must, of course, be rigorously dry. Since 1 grm. of formic acid reacts with 2·22 grms. of acetic anhydride $[(CH_3CO)_2O + H.CO_2H = 2CH_3.CO_2H + CO]$, while the melting point of the acetic acid is lowered by 0·38° C., if 1 per cent. of the anhydride is present, and by 0·8° C. if 1 per cent. of formic acid is present, it can be shown that the percentage of water E is given by:

$$\frac{0{\cdot}38(P - 2{\cdot}22F) \pm [A_1 - (A_2 - 0{\cdot}8F)]}{4{\cdot}15},$$

P being the weight of acetic anhydride taken per 100 grms. of the acid.

(4) The percentage of higher acids is given by the expression

$$2[16{\cdot}70 - (A_1 + 2E + 0{\cdot}8F)],$$

since 2 per cent. of these higher acids depresses the melting point of acetic acid by 1° C.

Application of these methods to a number of test samples of acetic acid containing various proportions of the different impurities has apparently given surprisingly exact results. Thus, a mixture with the percentage composition: formic acid 1·168, water 0·111, higher acids (70 per cent. of propionic and 30 per cent. of butyric) 2·60, and acetic acid 96·12, gave 1·169, 0·126, 2·66, and 96·05 per cent. of the respective constituents.

Other impurities may be tested for as follows: Mineral matter in the usual way; aldehydes by Schiff's reagent, which gives approximately quantitative results; furfural by means of aniline; empyreumatic substances by the brown coloration given with concentrated sulphuric acid or, better, by treating 5 c.c. of the acid with 15 c.c. of water and 3 c.c. of 0·1 per cent. potassium permanganate solution: the pink colour should persist for at least 15 minutes for the acid to be satisfactorily free from empyreumatic matter. T. H. P.

Oxidation of Dihydroxystearic Acid by Potassium Permanganate in Acetone. J. Bougault and G. Schuster. (*J. Pharm. Chim.*, 1932, **124**, 5–7.)—The only product of the oxidation of castor oil by means of Hilditch's method with potassium permanganate in boiling acetone solution, was found to be triazelain. Three per cent. of stearic acid, added to the castor oil before oxidation, was recovered almost quantitatively, but dihydroxystearic acid is oxidised in the same way as oleic acid, and 1·17 grm. of azelaic acid (theory, 1·18 grm.) was obtained by oxidising 2 grms. of dihydroxystearic acid (dissolved in 20 c.c. of acetone) by means of 4 grms. of permanganate. Therefore, the fact that only azelaic acid results from the oxidation of castor oil affords no proof of the presence or absence of dihydroxystearic acid in the original oil. Further, the iodine value will not necessarily afford any indication of the measure of oxidation; thus, a triglyceride of dihydroxystearic acid will give triazelain, and will behave like triolein, but the iodine value of the triolein will be 86, and that of dihydroxystearic triglyceride will be 0. D. G. H.

Iodimetric Method for the Determination of Citric Acid. P. A. Kometiani. (*Z. anal. Chem.*, 1931, **86**, 359–366.)—On the basis of the work of others (which is described) a method has been evolved in which the citric acid is oxidised to acetone dicarboxylic acid, and this is then brominated to give pentabromoacetone ($CHBr_2.CO.CBr_3$; m.pt., 73° C.; insoluble in water, but soluble in organic solvents). This reacts quantitatively with hydriodic acid in alcoholic solution, liberating 6 atoms of iodine per molecule, which may then be titrated. To a clear solution of 5 to 40 mgrms. of citric acid are added 1 c.c. of 1:1 sulphuric acid and 0·3 c.c. of 22·5 per cent. potassium bromide solution for each 10 c.c. present, though the final volume should not exceed 100 c.c. The mixture is heated at 40° to 45° C., and the citric acid is oxidised by addition, drop by drop, of a saturated solution of potassium permanganate until there is no further decolorisation, an excess being avoided to obviate oxidation of the acetone dicarboxylic acid to formic and oxalic acids. The bromine liberated at this stage also reacts, and the liquid turns yellow and then brown; the appearance of drops of oil on the surface of the liquid indicates the presence of bromination products due to an excessive temperature. After 5 minutes on the water-bath the solution is cooled and any free bromine or hydrated manganese dioxide is removed by addition of a saturated solution of ferrous sulphate containing 1 drop of sulphuric acid. The pentabromoacetone is allowed to settle for 1 hour, and is then filtered off on a Gooch crucible, washed with cold water, and finally dissolved in 25 to 50 c.c. of 96 per cent. alcohol, after which 5 c.c. of acetic acid are added. The mixture is heated almost to boiling, 5 c.c. of a 20 per cent. solution of sodium iodide in 96 per cent. alcohol are added, and, after 5 minutes on the water-bath and 10 to 15 minutes' cooling, the solution is diluted 10-fold with water, and the iodine is titrated with 0·1 *N* sodium thiosulphate solution, with 1 per cent. starch solution as indicator; then 1 c.c. ≡ 3·501 mgrms. of citric acid. Dilution sensitises the end-point by rendering the reaction between unsaturated organic compounds and hydriodic acid irreversible. The formation of pentabromoacetone may be used as a qualitative micro-reaction which has a sensitiveness of 1:100,000. Tests of the method on solutions containing 4 to 40 mgrms. of pure citric acid gave results 0·1 to 1·0 mgrm. low, the most accurate results being obtained with the largest quantities. The errors are slightly greater if acetone or methyl alcohol is used as solvent in place of ethyl alcohol.

Milk.—The sample (10 c.c.), diluted with an equal volume of water, is shaken with 2 c.c. of 1:1 sulphuric acid and 4 c.c. of a solution prepared by dilution to

2 litres of a mixture of 100 c.c. of 30 per cent. sulphuric acid and a solution in water of 120 grms. of disodium hydrogen phosphate and 200 grms. of sodium tungstate. The precipitate is removed by filtration after 1 minute, and is washed with a little cold water, and the method described above is applied to the filtrate. Cows' milk contained 1·8 to 2·0 grms. of citric acid per litre, the somewhat higher values (up to 4 grms. per litre) found by Schwaibold and others (*Milch Forsch.*, 1925, **2**, 306, 312) being explained by the inaccuracy of their methods; buffaloes' milk contained 3·0 to 3·5 grms. per litre. J. G.

Detection of Nitrocellulose in Coats of Paint or Lacquer. P. Slansky. (*Chem. Ztg.*, 1932, **56**, 20).—About 50 sq. cm. of the coating, cut into pieces, are extracted with acetone for about an hour in a Soxhlet apparatus. The extract is evaporated to 2 to 3 c.c. and diluted, in a test-tube, with 15 to 20 c.c. of chloroform. If the liquid remains clear, nitrocellulose is absent. Any nitrocellulose present separates as a jelly, which is filtered off, washed thoroughly with chloroform, and saponified with about 20 c.c. of 0·1 *N* sodium hydroxide solution. The alkaline solution is then tested for nitric acid with either diphenylamine and sulphuric acid or, better, ferrous sulphate and sulphuric acid.

If the coating consists of several layers, and it is desired to know which of these contains nitrocellulose, the separate layers are rubbed off with small pieces of filter-paper wetted with acetone, the papers being then extracted with acetone and the extracts treated as described above. In order to ascertain of how many layers the coating consists, a sample is treated gradually with either 0·1 *N* sodium hydroxide solution or acetone, which saponifies or dissolves the layers in turn. Even with pure oil paint or oil lacquer, the layers are removed separately, since they exhibit different velocities of saponification. Care must be taken that each layer is steeped with the alkali only until it is removable by moistening it with water and cautiously rubbing it. The above procedure naturally serves also for the detection of nitrocellulose in liquid paint—by extraction with acetone and dilution of the extract with chloroform. T. H. P.

Inorganic Analysis

Determination of Bismuth as Metal. E. Rupp and G. Hamann. (*Z. anal. Chem.*, 1932, **87**, 32–35.)—The high results experienced in the reduction with alkaline formaldehyde are shown to be due, not to alkali adsorption, but to presence of suboxide. The following procedure gives good results: The solution (not more than 0·3 grm. Bi) is heated on the water-bath with formaldehyde and excess of sodium hydroxide until the supernatant liquid is quite clear. It is then boiled after addition of more aldehyde, filtered through a tared filtering tube provided with an asbestos pad, the precipitate repeatedly washed by decantation with hot water, collected, washed with alcohol and ether, and dried. A current of dry hydrogen is passed through the tube, which is heated to between 200° and 250° C. for 5 minutes. After cooling in hydrogen, the tube is again weighed.

In Strecker and Herrmann's process (precipitation of metal by magnesium from weakly acid chloride solution) it was found best to proceed as follows: Neutralisation with sodium hydroxide until slightly turbid, addition of a minimum of acid to remove the turbidity, treatment with 3 grms. of Rochelle salt, and addition of 0·5 to 0·6 grm. of magnesium in small portions. After half-an-hour's heating, the turbid solution (basic magnesium salt) is cleared with ammonium sulphate solution, the free ammonia being expelled by boiling. The metallic bismuth is collected as before, washed, dried, and weighed. W. R. S.

Separation of Germanium and Arsenic. H. J. Abrahams and J. H. Müller. (*J. Amer. Chem. Soc.*, 1932, **54**, 86–94.)—A study has been made of the use of hydrogen sulphide for the separation of germanium and arsenic, which indicated that germanium does not precipitate as sulphide until the acid concentration of the solution exceeds 0·09 *N*. The following method was adopted in the test experiments: To the neutral solution (60 to 70 c.c.) containing germanium and (arsenious) arsenic, 3 c.c. of approx. 0·1 *N* sulphuric acid and 1 grm. of ammonium sulphate were added, and the mixture was saturated with hydrogen sulphide under pressure (presumably at the ordinary temperature). The arsenic sulphide was filtered off, washed with dilute ammonium sulphate solution containing hydrogen sulphide, and the arsenic was determined as magnesium pyroarsenate according to the directions of McNabb (*J. Amer. Chem. Soc.*, 1927, **49**, 1451). The filtrate containing the germanium was made 6 *N* in acidity with sulphuric acid, and the precipitate of germanium sulphide was filtered off on a sintered glass crucible and washed with a few c.c. of 2 to 3 *N* sulphuric acid saturated with hydrogen sulphide. The crucible was placed in a quartz beaker and covered with water, which was kept actively boiling until the germanium sulphide had dissolved, a cover glass being kept on the beaker to exclude air as far as possible, and thus prevent the formation of free sulphur. The crucible was then removed and the liquid was evaporated almost to dryness; a small quantity of nitric acid was added, the evaporation completed, and the residue ignited to germanium dioxide, in which form the germanium was weighed. There is some tendency for the arsenic sulphide precipitate to occlude germanium sulphide; the effect is negligible when the proportion of arsenic to germanium is small, but when it exceeds 15 to 20 per cent. the arsenic sulphide should be re-precipitated—the authors dissolved the arsenic sulphide in the minimum quantity of dilute ammonia (1:2), diluted the solution to 150 c.c., and added *N* sulphuric acid until the acidity of the solution was 0·05 to 0·1 *N*; the liquid was saturated with hydrogen sulphide, filtered, and the germanium in the filtrate was recovered by further acidification, etc., as described above. The method was used for the analysis of germanite. The germanium and arsenic in this material were first separated from the other constituents of the ore by distillation of the chlorides in hydrochloric acid; the arsenic and germanium in the distillate were separated as described. The results of a complete analysis of germanite were as follows: Ge, 7·37; As, 3·92; Cu, 45·38; Fe, 5·89; Ga_2O_3, 0·68; Al_2O_3, 0·13; Zn, 2·87; Pb, 0·71; S, 30·96; W, 0·10; gangue, 1·47 per cent. S. G. C.

Separation and Determination of Iridium. L. Moser and H. Hackhofer. (*Monatsh. Chem.*, 1932, **59**, 44–60.)—In the following processes of separation, iridium is precipitated by hydrolysis under oxidising conditions as greenish-black hydrated dioxide; precipitation is brought about by sodium bromide and bromate. *From platinum.*—The faintly acid chloride solution (maximum 0·3 grm. Pt, 0·1 grm. Ir; 200 to 400 c.c.) is treated with 1·5 to 2 grms. of sodium bromate at 60° C., and a slight excess of 10 per cent. sodium bromide solution, and boiled until the smell of bromine is no longer perceptible (about 45 minutes). Precipitation is complete if fresh addition of the two salts does not cause a cloudiness and an odour of bromine. The precipitate is left to settle on the water-bath, filtered on close-textured paper, and carefully washed with hot ammonium nitrate solution. The filtrate is tested for complete precipitation by concentration and renewed addition of reagents. Filter and precipitate are dried in a porcelain crucible covered with a perforated mica plate; a stream of hydrogen is introduced, and a temperature of 160° to 180° C. maintained for half-an-hour. This prevents decrepitation. The precipitate is cooled under hydrogen, heated in air for the destruction of the paper, ignited in hydrogen, and cooled in carbon dioxide. It is then leached several times with hot water acidified with nitric acid for the removal of adsorbed soda; after another ignition with the above precautions, it is weighed as iridium. The platinum in the filtrate is determined, after boiling with nitric acid for the destruction of the bromate, by precipitation with ammonium acetate and hydrazine hydrochloride. The ignited metal should be leached and re-ignited before the final weighing. *From gold.*—The above directions apply also to the separation of iridium from gold; the solution should be diluted to 600 c.c. or more, because filter paper adsorbs the gold salt unless the concentration is very low. *From palladium.*—The hydrolysis method is applied as before, but the ignited and reduced iridium must be subjected to further treatment, as it contains palladium. It is heated on the water-bath with *aqua regia* diluted with its own volume of water; after 3 to 4 extractions, it is collected, washed, ignited, reduced, and weighed. The palladium in the filtrate is precipitated with hydrazine after destruction of the bromate (*vide supra*). The weighed metal should be leached with hot water and re-ignited, as a precaution against adsorbed alkali chloride. *From copper.*—The hydrolysis precipitate obtained as before contains nearly the whole of the copper. It is dried and then heated for half-an-hour at 170° C. in a current of hydrogen. Filter and precipitate are then digested on the water-bath with nitric acid (100 c.c. water to 7 c.c. of strong acid) for half-an-hour; the solution is decanted through a filter and the extraction repeated. The iridium is collected, again treated with hydrogen at 170° C., cooled, ignited, reduced, and weighed. Freedom from alkali is ensured by leaching and renewed ignition. W. R. S.

Separation and Determination of Rhodium. L. Moser and H. Graber. (*Monatsh. Chemie*, 1932, 59, 61–72) (*cf.* preceding abstract).—Hydrolytic precipitation of greenish-black rhodium hydroxide by means of bromide and bromate is applied to the separation from platinum and gold. The weakly acid solution (neutralised, if necessary, with sodium carbonate) of the chlorides (0·003 to 0·1 grm. Rh, 0·003 to 0·3 grm. Pt; 300 to 400 c.c.) is treated with 30 c.c. of half-molar sodium bromate solution, then at 70° C. with molar sodium bromide solution. The liquid is boiled for an hour in the covered beaker; on being tested with more bromide and bromate, it should not evolve bromine on boiling. The precipitate is left to settle on the water-bath, collected, washed with hot ammonium nitrate solution, dried at 110° C., ignited in a porcelain crucible, reduced in hydrogen, cooled in carbon dioxide, and weighed. It is then leached, at boiling heat, with water acidified with hydrochloric acid, filtered off, washed free from chloride, again ignited with the same precautions, and weighed. A second test for adsorbed alkali is recommended. For the recovery of platinum in the filtrate, and the necessary dilution of the solution in the separation of gold from rhodium, the directions are the same as in the preceding abstract.

The method does not effect a separation of rhodium from copper or iron. *Copper.*—In the separation from copper the 0·1 *N* sulphuric acid solution, containing 15 c.c. of 0·1 molar magnesium chloride solution per 100 c.c., is treated with hydrogen sulphide, first at boiling heat, then at 90° C., and, finally, left to cool while the gas is passing. The precipitate is collected and washed free from sulphate with hydrogen sulphide water, ignited wet, transferred to a beaker, and extracted with 100 to 200 c.c. of nitric acid (1:1). After decantation, the extraction is repeated. The residue is collected, ignited in hydrogen, and cooled in carbon dioxide; the reduced metal is again extracted twice with strong nitric acid on the water-bath. The final residue is collected, ignited and reduced with the usual precautions, leached, ignited, reduced, and weighed as rhodium. *Iron.*—The separation from iron is based on the precipitation of rhodium as sulphide. The chloride solution (0·1 *N* concentration of hydrochloric acid; 200 to 400 c.c.) is treated with magnesium chloride and hydrogen sulphide exactly as in the separation from copper. The sulphide precipitate is ignited, reduced, etc., as before, and weighed as rhodium. W. R. S.

Determination of Tungsten in Steel as Hydrated Tungstic Acid. H. Wdowiszewski. (*Z. anal. Chem.*, 1932, **87**, 36–38.)—The yellow precipitate, obtained by solution of the steel in hydrochloric acid and subsequent oxidation with nitric acid, is usually ignited in platinum and weighed as WO_3 (factor, 0·7931). The precipitate may, however, be collected on asbestos in a Gooch crucible, washed with 2 per cent. hydrochloric acid, then twice with alcohol, dried at 100° to 110° C., and weighed as H_2WO_4 (factor, 0·736). The results are close, and the method is advantageous in saving wear of the platinum crucible. In the subsequent analysis of the precipitate (always necessary in accurate work), fusion is obviated; the weighed precipitate is washed with hot dilute ammonia, in which it is soluble, leaving silica and ferric (chromic) oxide insoluble. The filtrate is treated with a small excess of sulphuric acid and benzidine solution in the usual manner.

W. R. S.

An Overlooked Source of Error in the Ferrocyanide Titration of Zinc. B. Park. (*J. Amer. Chem. Soc.*, 1932, **54**, 180–181.)—When a ferrocyanide solution is kept a small proportion of ferricyanide is formed. Whereas in the ferrocyanide method for determining zinc, as described by, *inter alios*, Low, *Technical Methods of Ore Analysis*, hydrogen sulphide is added to the zinc solution before the titration with ferrocyanide, the standardisation of the ferrocyanide solution is carried out by titrating a standard solution of zinc in the absence of hydrogen sulphide. A hitherto unsuspected error is liable to arise owing to the reduction of any ferricyanide in the ferrocyanide solution by the hydrogen sulphide, thus increasing the ferrocyanide content of this solution as determined in the standardisation. Thus, the author has found (1) that the zinc equivalent of a ferrocyanide solution altered from 0·00532 to 0·00524 grm. of zinc per c.c. on keeping for seven years; (2) that this old ferrocyanide solution had a greater zinc equivalent in the presence than in the absence of hydrogen sulphide in the zinc solution titrated (38·18 c.c. and 39·65 c.c. of ferrocyanide solution, respectively, for 0·2490 grm. of zinc). Only a slight difference was detected in the zinc equivalent of a fresh ferrocyanide solution in the presence and absence of hydrogen sulphide (39·15 c.c. and 39·33 c.c. of ferrocyanide solution, respectively, for 0·2490 grm. of zinc). It is, therefore, recommended that hydrogen sulphide be also added to the zinc solution used for the standardisation. S. G. C.

Determination of Manganese by Means of Persulphate. R. G. Harry. (*J. Soc. Chem. Ind.*, 1932, **51**, 24T.)—The precipitation of manganese by ammonium persulphate was carried out in presence of about 4 per cent. of various other metals, the sulphate solution, containing 10 c.c. of 20 per cent. sulphuric acid in 500 c.c. total bulk, being boiled and treated with 50 c.c. of fresh 12·5 per cent. persulphate solution; after 20 minutes' boiling, the same quantity of persulphate was again added. The washed manganese peroxide was dissolved in a known excess of acid ferrous sulphate solution; the excess of ferrous iron was ascertained by dichromate titration. It was found that copper, lead, zinc and calcium were without influence in this procedure. High results were obtained in presence of titanium, bismuth, tin, vanadium and cobalt; whilst antimony, arsenic, nickel, and tungsten caused the results to be low (*cf.* ANALYST, 1932, 125). W. R. S.

Determination of Manganese as Manganese Ammonium Phosphate. P. Nuka. (*Z. anal. Chem.*, 1932, **87**, 7–26.)—The most favourable conditions for the formation of a precipitate of correct composition and the choice of the most suitable wash-liquor for the precipitate were re-investigated. The conclusion is, that hot one per cent. diammonium phosphate solution, followed by 60 to 65 per cent. alcohol, is the best wash-liquor; if the phosphate is produced as a flocculent precipitate which becomes crystalline only on warming, variable results and positive errors ensue. More constant results, in closer agreement with calculated values, are obtained by gradual precipitation of the crystalline modification. The boiling, neutral solution, free from sulphates and containing 15 to 20 grms. of ammonium chloride, is stirred and treated, drop by drop, with 50 c.c. of 2 per cent. diammonium phosphate solution; 25 c.c. of 6 per cent. solution of the same salt are then added more quickly. Acetates do not interfere. W. R. S.

Determination of Aluminium. Formation of Lithium Aluminate. J. T. Dobbins and J. P. Sanders. (*J. Amer. Chem. Soc.*, 1932, **54**, 178–180.)—To a solution of aluminium nitrate (100 c.c.) were added a few drops of phenolphthalein indicator, and lithium chloride solution (10 per cent.) "in excess of that required to precipitate the estimated amount of aluminium in the sample." Ammonia was added, drop by drop, with stirring, until the solution became a faint pink. The voluminous precipitate was allowed to settle for 5 minutes, filtered off (it is stated to filter readily), washed with water until free from chloride, and, after preliminary drying, ignited, at a high temperature, to constant weight; the residue was weighed, and the aluminium was calculated from the formula $2Li_2O,5Al_2O_3$. The process, tested on amounts of aluminium of the order of 0·1 grm., gave good results. No independent verification of the formula of the lithium aluminate produced in this method appears to have been carried out. The statement made in the summary of the work, that the process yields more concordant results than the ammonium hydroxide method, is not supported by experimental data.

S. G. C.

Microchemical

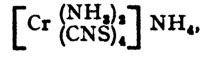
Microchemical Examination of Pictures. H. Hetterich. (*Mikrochem.*, 1932, 10, 27–44.)—*Examination of Media.*—The protein group of media, such as protein, egg yolk, glue (size) and casein, contain nitrogen, whilst the dry oils (such as linseed oil), the waxes, starch, dextrin, cherry gum, gum arabic, and others contain no nitrogen. Emich's (Emich, *Mikrochemisches Praktikum*, 1931, p. 106) test for nitrogen is used to distinguish the two groups; the organic compound is heated with precipitated lime in a thin-walled capillary tube, sealed at one end. The ammonia developed on heating changes the colour of a litmus paper (soaked in litmus containing $N/20$ acid) at the open end. The test is sensitive to 0·1γ of nitrogen. Small amounts of pigment, with the exception of indigo and Paris blue, do not interfere with the test. The proteins of the nitrogen-containing group of media also contain sulphur, for which the Grünsteidl test (*Z. anal. Chem.*, 1929, 77, 283) is used, in which the sulphur is converted into sulphide by heating with sodium hydroxide in a micro porcelain crucible. By further evaporation with 0·1 per cent. potassium cyanide solution the thiocyanate is formed, and this gives the usual red colour with ferric salts. When much phosphorus is present, as in casein, Feigl's test (Feigl, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen*, 1931, p. 282) for sulphides is preferable, in which bubbles of nitrogen are formed when a drop of iodine nitride reagent (100 c.c. of 0·1 N iodine containing 3 grms. of sodium nitride) is added to a drop of a sulphide solution. The presence of phosphorus is used as a test for casein. The compound is oxidised with concentrated sulphuric acid and perhydrol to phosphoric acid, which is identified by the blue colour produced on adding ammonium molybdate solution in nitric acid, and then benzidine. Silicic acid (which may come from the walls in wall paintings) interferes with this test, but can be rendered inert by carrying out the test in the presence of ethyl alcohol. The "fatty oils" of the nitrogen-free media are identified by the conversion of the glycerol grouping into acrolein, by heating with solid alkali and sodium bisulphate in a thin-walled capillary tube. The acrolein vapour is identified by the red coloration of acid Schiff's reagent (0·1 grm. of fuchsin and 0·7 grm. of sodium bisulphite in 88 c.c. of water, treated, after an hour's standing, with 25 drops of concentrated sulphuric acid). *p*-Nitro-phenylhydrazine hydrochloride in aqueous solution, containing a little dilute acetic acid, is also used for the test; a small drop is drawn into a fine capillary, which is placed inside the capillary in which the acrolein is developed, so that the vapour passes through the solution, when orange-coloured crystals of the osazone, which can be seen under the microscope, are formed. The "fatty oils" may also be saponified on the microscope slide with alcoholic potash, but the crystalline products are all similar.

Examination of Pigments.—Feigl's "spot" test methods (vide *supra*) and the usual microscopic methods are used for the identification of the pigments. An example is given of a detailed analysis of the painting on a wooden Madonna statue of 1620 A.D. Six different layers, of total thickness 0·6 mm., of which 0·1 mm. was pigmented, were distinguished in a cross section under the microscope. These were separated and analysed. The bottom layer was calcium carbonate, calcium sulphate and glue or size; the second layer, calcium carbonate and glue; the third, azurite, white lead and gum arabic; the fourth, ultramarine and white of egg; the fifth, azurite and oil (or tempera rich in oil), and an oil varnish (*cf.* Laurie, ANALYST, 1930, **55**, 162). J. W. B.

A New Cymene Bath for Pregl's Micro-Combustion. A. Verdino. (*Mikrochem.*, 1931, 9, 123–125.)—A new cymene bath ("Hohlgranate") for maintaining the lead peroxide of the combustion tube at constant temperature is described. A safety device renders it less likely to boil over or catch fire than with the old model. The outer dimensions are the same (obtainable from P. Haack, Vienna). J. W. B.

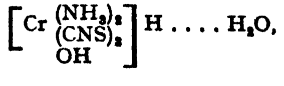
Electric Heater for Pregl's Micro-Combustion. W. Füner. (*Mikrochem.*, 1932, **10**, 66–69.)—A simple electric heater for micro-combustion consists of a heater, 19 cm. long (to replace the long burner), made of nickel-chromium wire covered with kieselguhr, taking 1·3 to 2 amp. of current, which will heat the oxidising portion of the tube to red heat. The cymene bath is replaced by an electric heater, 7 cm. long, made of a block of iron which can be maintained at 174° to 176° C. This uses a current of 0·5 amp. when heating, and remains constant with 0·35 amp. An Osram iron resistance lamp (0·35 amp.) is used in the circuit to maintain the evenness of the current. The advantage of the electric constant-temperature heater is that it can be kept running indefinitely, with no danger of fire or of fumes of cymene escaping into the air. The Bunsen burner is retained for the heating of the substance in the boat, as the process of combustion is easier to watch, and the tube cools more quickly for a subsequent determination. [The heater is obtainable from Firma Kirchenbauer (Apparatebau), Singen (Pforzheim).] J. W. B.

Tests for Nicotine in the Presence of Pyridine and its Derivatives. R. Hofmann. (*Mikrochem.*, 1932, **10**, 53–56.)—1. *With hydroxy-tri-thiocyanate di-amino chromic acid*—The reagent is prepared from Reinecke's salt,



$$\left[\mathrm{Cr}\begin{matrix}(\mathrm{NH_3})_2\\(\mathrm{CNS})_4\end{matrix}\right]\mathrm{NH_4},$$

by recrystallising three times from a dilute acetic acid solution, and then dissolving 1 grm. of the purified salt in 5 c.c. of 8 per cent. hydrogen peroxide solution. The reagent,



$$\left[\mathrm{Cr}\begin{matrix}(\mathrm{NH_3})_2\\(\mathrm{CNS})_3\\\mathrm{OH}\end{matrix}\right]\mathrm{H}\ldots\ldots\mathrm{H_2O},$$

(Werner's acid, *Ber.*, 1916, 49, 1539) is used in the form of a saturated solution. When a drop of the neutral or slightly acid solution under examination is placed on a microscope slide with a drop of the reagent, large leaf-shaped crystals are formed in the presence of nicotine. The smallest amount recognisable is 0·157γ in a dilution of 1:3800. Pyridine also gives crystals with the reagent, and, although these differ in form from those given by nicotine, yet, with increasing concentrations of pyridine, the two forms become indistinguishable. The highest percentage of pyridine that can be present for the test to be successful is 75 per cent.; of collidine, 90 per cent.; of lutidine, 75 per cent.; and of picoline, 75 per cent. 2. *With silico-tungstic acid.*—The slightly acid (0·1 to 1 per cent. of hydrochloric acid) solution under examination is mixed with a drop of 10 to 12 per cent. sodium silicotungstate. According to the concentration, a cloudiness or white precipitate is formed; if the latter, the solution should be diluted. A few granules of sodium chloride are then added, and in 5 or 10 minutes the nicotine crystallises out in rectangular plates, which are not doubly refracting. The smallest amount recognisable is 0·4γ in a dilution of 1:1,250,000. Pyridine forms larger, more diffractive crystals; lutidine, picoline and collidine do not form characteristic crystals. Photomicrographs of the different crystals are given. J. W. B.

Microchemical Test for Hydrogen Peroxide and for Vanillin. C. Griebel. (*Mikrochem.*, 1931, 9, 313–315.)—Vanillin hydrochloride forms a blue crystalline compound with hydrogen peroxide. The reaction is used as a test for peroxides, a drop of the solution, or a few granules of the solid, being added to a drop of a 1 per cent. solution of vanillin hydrochloride (0·1 grm. of vanillin dissolved in 10 grms. of 25 per cent. hydrochloric acid and warmed). In 5 or 10 minutes the liquid, if hydrogen peroxide is present, becomes reddish-brown, and, finally, feathery groups of blue-black or violet-black needles crystallise out. Better crystals are formed when the vanillin solution contains alcohol (0·1 grm. of vanillin in 1 c.c. of alcohol and 9 c.c. of 25 per cent. hydrochloric acid). The smallest amount of hydrogen peroxide recognisable in an aqueous solution of 0·02 c.c. volume is 25γ. This test is not so sensitive as the iodine test, but it is specific, and is not interfered with by the presence of other oxidising agents, as is the iodine reaction. *Vanillin.*—As little as 23γ of vanillin can be detected by the test. J. W. B.

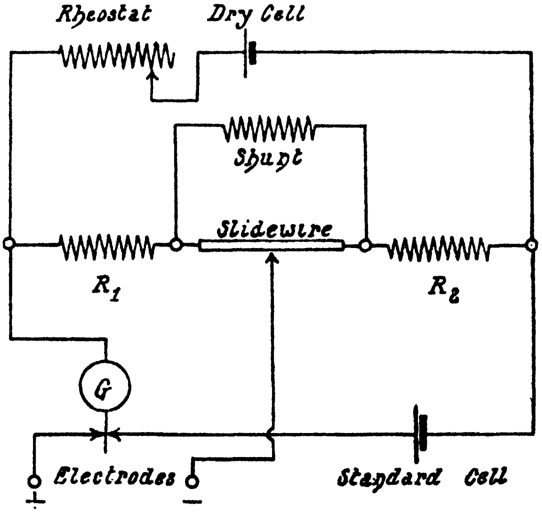
Physical Methods, Apparatus, etc.

Drawing Reproduction and Lantern-slide Making. H. C. Bennett and R. Lee. (*J. Chem. Education*, 1931, 8, 2208–2211.)—Kodalith, a new Eastman paper, which has extreme contrast and shows no texture, is recommended for the reproduction of graphs by direct contact. The graphs should be drawn on tracing cloth and a negative prepared on Kodalith. Paper negatives on Kodalith can also be used for the preparation of lantern slides of graphs or typewritten tables of figures. "Slow" lantern plates should be used.

Methods for Studying the Scale Structure of Animal Fibres. J. I. Hardy. (*J. Text. Inst.*, 1932, 23, 1T.)—The difficulty of observing the scale structure of medullated and pigmented fibres can be overcome by making a celloidin cast of the hairs or fibres and examining this under the microscope. The method consists in fastening the fibres parallel, without touching each other, over a shallow trough and pouring over them a 20 per cent. solution of celluloid in acetone. After drying for a short time, the celluloid is peeled off, the fibres pulling through the cast and leaving a fissure which does not interfere with the microscopic examination. A series of photomicrographs is given showing the type of result obtained by this method.

Method for Revealing Scale Structure of Wool and Hair. J. Manby. (*J. Text. Inst.*, 1932, **23**, 15T.)—This method is devised to overcome the difficulty that, in examining hairs, the out-of-focus image of the lower scales often interferes with the observation of the upper scales and *vice versa*. The author makes use of the fact that the image of the lower scales can be caused to disappear by mounting the fibres so that the lower half of the fibre is immersed in a medium of approximately the same refractive index as the fibre, but at the same time keeping the upper surface of the fibre clean so that the visibility of these scales is not affected. The method consists in laying the hairs on a glass slide and placing a small drop of the mounting medium at one end and allowing it to drain along the fibre. No cover glass must be used in observing the fibre under the microscope. The mounting medium recommended is composed of 3 grms. of gelatin, 3 grms. of glycerin, and 94 c.c. of water, plus a little phenol or thymol as a preservative. Methods of microscopical technique are discussed and photomicrographs are given.

Automatic *p*H Recorder. C. Morton. (*J. Soc. Chem. Ind.*, 1931, **50**, 436–438T.)—The cell (see Figure), which is made of ebonite, bakelite or porcelain, consists of three compartments with inlets at the top and outlets at the bottom, separated by two porous diaphragms, and containing the sample, saturated potassium chloride solution, and a buffer solution of known *p*H value (*A*), respectively. Two guide-rods, passing lengthwise through all three compartments, keep them in close contact, the completed assembly being held together by means of a screw-clamp, the jaws of which fit into recesses in the end-plates; rubber washers ensure water-tight contacts. Replaceable gold or platinum electrodes, the areas of which are such that the resistance of the cell is approximately equal to that of the galvanometer coils (2,000 ohms), are washed in acetone or ignited over a spirit lamp and mounted in rubber bungs which are then inserted in the end-compartments. For continuous measurements the main supply of sample is conducted



through a siphon-chamber (serving as a by-pass), containing a bag of quinhydrone, from which it overflows into a small cistern (to enable the siphon to act at atmospheric pressure), and thence enters the first compartment. Similar devices attached to reservoirs containing the appropriate solutions (not shown) supply the other two compartments, and ensure automatic flushing. Then pH (at 18° C.) = $(E/0{\cdot}058) \pm A$ (accuracy and "lag" not stated). The surface of the cell should be clean and dry, and care should be taken that the system is not earthed by potassium chloride drippings at the drain outlet. The (Cambridge) recording outfit has the usual potentiometer circuit, but the galvanometer, on deflection, activates a pre-set mechanical relay which moves the slide-wire contact so as to balance the system and thus reduce the deflection. The circuit is thus maintained in balance between limits pre-determined by adjustment of the bridge resistances, the sliding-contact being connected with a recording pen or warning signal. J. G.

Reviews

PRAKTIKUM DER WARENKUNDE. EIN HILFSBUCH FÜR DIE CHEMISCH-PHYSIKALISCHE UND MIKROSKOPISCHE WARENPRÜFUNG. By EDMUND GRÜNSTEIDL, Ph.D. Pp. 196, with 215 illustrations. Vienna: Julius Springer. 1931. Price RM. 11.50.

This is intended as a laboratory guide for a general course for commercial students. For many years the teaching of scientific method to others than those who intend to make it their life's work has been recommended in this country, and this book would appear to be the result of a similar intention in Germany. After a careful perusal the reviewers are not sure that, after all, such efforts can lead to results as useful as was at first hoped.

This book deals with such varied articles as metals, glass, dyes, textiles, oils and foodstuffs. The tests suggested are usually of the simplest description; thus, under Milk, we have only those for specific gravity, the addition of neutralising substances and pasteurisation; and margarine is distinguished from butter by means of a test for sesamé oil. It may be that such elementary work is of value in widening the merchant's outlook, if coupled with carefully arranged lectures, but, after all, it is not necessary to be a second-rate bricklayer in order to appreciate the efforts of the architect, and the question arises whether general lectures in scientific method, coupled with laboratory work of a less specialised kind, would not be of much greater value as a means of acquiring an appreciation of the scientist's outlook.

The printing, paper and general appearance of this book are particularly attractive, and the illustrations are carefully selected and excellently reproduced. The section on microscopy occupies more than half of the total space, but, as an introduction to the subject, suffers from the drawback that it deals too much with actual materials and too little with general principles. Thus, whilst excellent illustrations are given of textiles, starches, sections of plants and powders, no detailed explanations or drawings are given of the different kinds of structure which can be recognised by means of the microscope.

The book will scarcely prove either interesting or useful to any class of British students, but that this is so cannot be regarded as a matter of concern.

G. D. ELSDON.
J. R. STUBBS.

PRACTICAL MICROSCOPY. By L. C. MARTIN, D.Sc., and B. K. JOHNSON. Pp. viii+116, with 88 figures, including 10 plates. London: Blackie & Son. 1931. Price 3s. 6d. net.

This small volume is intended as a guide to the technique of microscopy and photomicrography, and contains much matter that would be obtainable only with difficulty elsewhere. The contents are divided into thirteen chapters, and embrace a wide range of tables, formulae, and methods of utility in the technique of modern microscopy, including magnification, mechanical and optical parts of the microscope, numerical aperture, methods of illumination, photomicrography, the preparation of specimens of various kinds, polarised light, ultra-violet microscopy, and a final highly important chapter on the interpretation of the image observed. It will be obvious from the size of the volume that some of the subjects, notably the preparation of specimens, have been treated briefly, but the methods given are of wide application, and, although concise, are lucid and sound. Numerous references are given throughout the volume to sources of further information on various subjects, and the many illustrations are particularly useful, being well selected and adequately described in the text, whilst the index, which might perhaps be extended with advantage, is almost free from error. The book is thoroughly reliable, eminently useful, and should be in daily demand by the practical microscopist and photomicrographer.

The authors and publishers are to be congratulated upon their joint efforts in producing at such a reasonable price this excellent handbook, the merits of which, when known, will undoubtedly ensure a wide circulation. T. J. WARD.

COLLOID CHEMISTRY—THEORETICAL AND APPLIED. By Selected International Contributors. Collected and Edited by JEROME ALEXANDER. Volume III. First Series of Papers on Technological Applications. Pp. 655. New York: The Chemical Catalog Company, Inc. 1931. Price $10.50.

Volume II of this series was reviewed in THE ANALYST (1929, **54**, 263). Technical chemists have awaited with very considerable interest the appearance of the two volumes devoted to technological applications. The first of these now appears, with 42 papers by distinguished authors, who outline the present position of those colloid subjects on which they are recognised specialists.

Technological applications have been divided into four groups, and the first two occupy the present volume. As the editor states: "The first group consists of subjects of interest to many industries, and comprises eleven papers on *general principles* and six papers dealing with *mechanical* or more specialised matters. The second group (twenty-five papers) may, for want of a better name, be termed *telluric*; for it deals with matters which are of the earth, earthy, beginning with geology and mineralogy, and running to metals, petroleum, asphalt and agriculture."

The first paper is by McBain and Jerome Alexander on "Cohesion and Adhesion," and ably summarises the investigations of the last few years. Clark follows with a paper on "Some Practical Results of X-ray Researches on Colloids." This is well done and provides a useful summary of quite recent work.

The next paper, by Bartell, dealing with the wetting of solids by liquids, is excellent, and it will serve to clarify ideas on the complicated, but most important, subject of wetting. He distinguishes between adhesional wetting, spreading wetting and immersional wetting, and includes a good discussion of contact angles. Wetting phenomena are further treated by Von Terzaghi (The Influence of Elasticity and Permeability on the Swelling of Two-Phase Systems) and by Buchanan, who discusses flotation.

The wide range of subjects is reflected in the papers dealing with catalysis, adsorption by silica gel, colloid factors in water supply, grinding, electrical precipitation of suspensoids, the super-centrifuge, filtration, chemical warfare, colloid phenomena in glass, minerals, geology, porcelain, and sodium silicate solutions, corrosion, colloidal fuel, and coal tar. Such names as E. F. Armstrong, H. S. Taylor, Chwala, Liesegang, Silverman, Benedicks, U. R. Evans, Newton Friend, and Acheson show that the proper authorities have been chosen to review current research.

Washburn discusses ceramic refractories, Searle the colloidal nature of cements and mortars, Alexander, Guertler, Benedicks, Honda and Yap the questions of metals. Three papers are devoted to petroleum, and some over-lapping is the result; but it is interesting to have the views of Dunstan, Morrell and Egloff, and Gurwitsch. The nature of asphalt is treated by Nellensteyn.

The volume closes with a long paper by Gortner under the title: "The Colloid Chemistry of Wheat, Wheat Flour and Wheat-Flour Products." This is a particularly able summary, covering a wide range of subjects.

Mr. Alexander is to be congratulated on getting together so many experts from many countries. One can readily guess at his trials as editor. However, it must be conceded that he has done his part well, and the present volume is a worthy successor to the previous volumes. Criticisms there must inevitably be, but no one scientist could take it upon himself to criticise in detail colloid questions in so many and such diverse fields. The present reviewer has carefully examined those papers coming within the purview of his own interests, and is satisfied. One minor criticism may be permitted. Due, no doubt, to the difficulty of synchronising the receipt of so many papers, there is evidence that some of them are considerably behind work done in 1930–1931. Consideration of the references furnished at the ends of the papers will bear this out.

Taken altogether, this book deserves a place in the library of all chemists who are interested in colloid chemistry and its industrial applications. It is well printed and bound, and typographical errors are few. WILLIAM CLAYTON.

CHEMICAL EMBRYOLOGY. By JOSEPH NEEDHAM, M.A., Ph.D. Vol. I, pp. xxii+613+10 plates. Vol. II, pp. xvi+615–1253+3 plates. Vol. III, pp. xvi+1253–2021+1 plate. Cambridge: University Press. 1931. Price 105s. net.

Embryology has hitherto been regarded as a branch of morphology or anatomy, and no collective work, with the exception of Preyer's small book, entitled *Special Physiology of the Embryo* (1880), has so far been written, which would survey the numerous investigations (Dr. Needham's bibliography, pp. 1728–1970, contains more than 4500 references) on the development of the embryo from the chemical point of view. Chemical embryology has thus so far lived an intra-uterine existence in scientific journals and specialised monographs. It required a first-class obstetrician to bring chemical embryology into the world. This laborious and difficult task has been most skilfully performed by Dr. Needham, who is already well known as the author of *The Sceptical Biologist,* a work which in centuries to come will probably rival *The Sceptical Chymist* in importance to the history of science. Dr. Needham seems in the habit of producing classics, and there is no doubt whatever that *Chemical Embryology* is, and will remain, a classic for many years.

From the prolegomena (pp. 1–4) to the epilegomena (pp. 1613–1665) the work is impregnated with the idea that scientific knowledge comes gradually to maturity as the result of the accumulated labours of many observers, careful, though in many cases obscure; chemical embryology has certainly been built up by a host of enthusiastic workers who deserve our greatest admiration. Anybody who reads the first two parts (pp. 7–231) of Dr. Needham's treatise, dealing with the historical aspect of the question, will carry away admiration for the many scientists and philosophers and their critics who have helped in building up embryology in general, and chemical embryology in particular. It is the work of pioneers in a field hitherto unknown to many. Again, one may predict that these two sections will, for years to come, remain a history of the subject.

Before dealing with the main section of this work, namely, Part III (pp. 231–1613), one may, perhaps, be permitted to offer some criticism of the manner in which the historical aspect has been dealt with. Dr. Needham commits the common error of the zealous historian, of putting modern ideas into the interpretation of ancient observations. Such dangers must always be guarded against, and one cannot but feel that Dr. Needham has been sometimes misled by ascribing much to the past that really belongs to the present. Incidentally, reference must be made to a curious statement on p. 183. Dr. Needham writes with reference to Boerhaave's *Elementa Chemiae,* that "it will be noted that they are cast in the form of lectures or addresses, as if they had been taken down direct from the lectures of the Professor, a fact which gives them a peculiar charm, when it is remembered how many great men must have listened to them. . . ." Now the *Elementa Chemiae* (Dr. Needham writes *chymiae* on p. 183, but correctly *chemiae* on p. 1750) are not written as *if* they were lectures delivered by Boerhaave, but they are the actual lectures given by him. They were originally published in 1724, without Boerhaave's permission, under the title *Institutiones et Experimenta Chemiae,* but, as they contained too many personal attacks against Van Helmont, Paracelsus and others, Boerhaave republished these lectures under the title *Elementa Chemiae.* Dr. Needham quotes the 1732, Leyden edition, and he must thus have overlooked Boerhaave's *autographed* authority on the back of the title-page of Vol. I. The reviewer trusts he will be forgiven this minor criticism; after all, he has not come only to praise the author of *Chemical Embryology!*

Part III, entitled "General Chemical Embryology," constitutes the bulk of the work. A gigantic undertaking, which, had Dr. Needham not listed in his bibliography (p. 1878) that his *Ing. Diss.*, Cambridge, appeared in 1924, could easily be mistaken for the work of a lifetime. Dr. Needham tells us, however, in his

"Acknowledgments of Indebtedness," that the idea of writing his *Chemical Embryology* originated in 1923 during a conversation with Professor Sir F. G. Hopkins, and thus only nine years have been occupied in the production of this formidable book.

The section, "General Chemical Embryology," is divided into: (i) The unfertilised egg (for some reason or other Dr. Needham has excluded fertilisation from his treatise, a point which will be regretted by many); (ii) and (iii) Embryonic growth (pp. 368–615); (iv) Respiration of the embryo (pp. 615–777); (v) Ontogenesis and its biophysical phenomena (pp. 777–839); (vi–xiii) Embryonic metabolism, including carbohydrates, proteins, nucleins, fats, lipoids, sterols and inorganic constituents (pp. 839–1289); (xiv–xvii) Enzymes, hormones, vitamins, and pigments in ontogenesis (pp. 1289–1383); (xviii) and (xix) Immunology in the life of the embryo (pp. 1383–1456); (xx–xxii) The biochemistry of the placenta (pp. 1456–1565); (xxiii) Blood and tissue chemistry of the embryo (pp. 1565–1595); and (xxiv) Hatching and birth (pp. 1595–1613). This brief summary obviously does not do justice to the work, but it shows the extent of its undertaking. Biologists of all kinds of shades will turn to it for information and find it. The importance of an accurate knowledge of chemical events in the life of the embryo is well realised, and to have all this information at hand will be welcome to the student of genetics, the biologist, the agriculturist, the stock-raiser, the entomologist and the agronomic expert. The Subject Index (pp. 1917–2012) and the "Index Animalium" (pp. 2013–2021) will be found of real assistance. They should be consulted with care. The embryology of the chick has attracted interest since ancient times, and one naturally finds numerous references to *Gallus domesticus*. Compared with it, *Homo sapiens* makes a very poor show in Dr. Needham's "Index Animalium."

Science in general, and biochemistry in particular, are under a very real debt to Dr. Needham for his wide reading, his ability as a writer and scientist, and his great patient industry. The expression of gratitude to Dr. Needham is, however, not complete without a tribute to the Cambridge University Press for the care they have given to the production of this monumental work.

M. NIERENSTEIN.

Publications Received

THE B.D.H. BOOK OF P.P.P. STANDARDS. (Obtainable on request from The British Drug Houses, Ltd., Graham Street, N.1.)

APPLIED CHEMISTRY. Vol. II. FOODS. By C. K. TINKLER and H. MASTERS. London: Crosby, Lockwood & Son. Price 15s. net.

AN INTRODUCTION TO BIOCHEMISTRY. By R. J. WILLIAMS. London: Chapman & Hall. Price 21s. net.

HANDBUCH DER PFLANZENANALYSE. Band II. Spezielle Analyse. 1st Teil. Vienna: J. Springer. Price RM.96.

INDUSTRIAL CHEMICAL CALCULATIONS. By O. A. HOUGEN and K. M. WATSON. London: Chapman & Hall. Price 28s. net.

THE GLYCOSIDES. By E. F. ARMSTRONG and K. F. ARMSTRONG. London: Longmans, Green & Co., Ltd. Price 12s. 6d. net.

APRIL, 1932 Vol. LVII., No. 673

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Friday, March 4th, the President, Dr. J. T. Dunn, being in the chair.

Certificates were read for the first time in favour of:—Edward Bertram Anderson, M.Sc., F.I.C., Edward Foster Eaton, Frank Maudsley, B.Sc., F.I.C., Samuel Gordon Stevenson, B.Sc., B.Pharm., F.I.C., and James William Thom, B.Sc.

Certificates were read for the second time in favour of:—Alan Arthur Douglas Comrie, B.Sc., A.I.C., Edwin William Stanley Press, B.Sc., A.I.C., and Muriel Roberts, B.Sc., F.I.C.

The following were elected Members of the Society:—Albert Green, M.C., M.Sc., Ph.D., F.I.C., John Farrar Hardwick, B.Sc., A.I.C., Ernest Stephen Hawkins, B.Sc., A.R.C.S., F.I.C., Joseph Robert Johnson, F.I.C., M.Inst.M.M., Arthur Pillans Laurie, M.A., D.Sc., F.R.S.E., and John Morgan Tucker, B.Sc., A.I.C.

The Annual General Meeting of the Society then followed, when the President, Dr. J. T. Dunn, delivered his Presidential Address.

The following were elected as Officers and Council for the year **1932**:

President.—F. W. F. Arnaud.

Past Presidents, serving on the Council.—E. Richards Bolton, A. Chaston Chapman, J. T. Dunn, Bernard Dyer, Edward Hinks, P. A. Ellis Richards, G. Rudd Thompson, J. Augustus Voelcker.

Vice-Presidents.—H. M. Mason, G. W. Monier-Williams, G. Stubbs.

Hon. Treasurer.—E. B. Hughes.

Hon. Secretary.—G. Roche Lynch.

Other Members of Council.—A. L. Bacharach, H. E. Cox, E. M. Hawkins, A. E. Johnson, W. G. Messenger, H. H. Bagnall, W. T. Burgess, G. D. Elsdon, John Evans, L. Eynon, J. R. Nicholls.

Death.

With great regret we record the death, on March 17th, of Sir William Smith, who had been a Member of the Society since 1892.

Anniversary Dinner

The Society of Public Analysts and Other Analytical Chemists held a Dinner at the Trocadero Restaurant, on March 4th, to celebrate the 56th Anniversary of the foundation of the Society.

The members and their guests, numbering over 100, were received by the President, Dr. J. T. Dunn, F.I.C., and Mrs. Dunn, and Dr. Dunn afterwards took the chair at the Dinner.

The guests of the Society included the Rt. Hon. Lord Atkin, P.C., D.C.L. (Lord of Appeal), Councillor J. G. Nixon, J.P. (Lord Mayor of Newcastle-upon-Tyne), Sir Ernley Blackwell, K.C.B. (Assistant Under-Secretary, Home Office), Mr. A. T. A. Dobson, C.V.O., C.B.E. (Assistant Secretary, Ministry of Agriculture and Fisheries), Sir F. Gowland Hopkins, D.Sc., F.I.C., P.R.S., Professor G. T. Morgan, O.B.E., D.Sc., F.I.C., A.R.C.S., F.R.S. (President of the Society of Chemical Industry), Mr. Percy Gates (President of the Institute of Brewing), Mr. George Gray, M.Sc., F.I.C., M.I.Chem.E. (Vice-President of the Institution of Chemical Engineers), Sir Ernest Graham-Little, M.D., F.R.C.P., M.P. for the University of London, Mr. Norman Kendal, C.B.E. (Assistant Commissioner of Police), Mr. A. W. Monro, C.B. (Ministry of Agriculture and Fisheries), and Mr. R. B. Pilcher, O.B.E. (Registrar of the Institute of Chemistry).

After the toasts of His Majesty the King and the Members of the Royal Family had been honoured, the President proposed the health of the Members of H.M. Civil Service. Dr. Dunn emphasised the harmonious relations which existed between those branches of the Civil Service which were intimately associated with the work of Public Analysts and Official Agricultural Analysts, and he described H.M. Civil Service as one of the great causes of the stability of this country, and as the object of envy and respect of other nations.

Sir Ernley Blackwell, replying to the toast, referred to the connection between the Home Office and the Society, and said that it was almost fifty years since the first two Official Analysts to the Home Office were appointed. He recalled the fact that one of the most distinguished of these analysts was the late Sir Thomas Stevenson, a former President of the Society. He pointed out that the evidence in Court that was based on the facts provided by analysis was, as a rule, accepted by both sides, though the inferences to be drawn from those facts were sometimes challenged.

Mr. A. T. A. Dobson also replied to the toast, and referred to the friendly relations existing between the Ministry of Agriculture and the Society of Public Analysts. He said that cases in which permission to prosecute was given by the Ministry of Agriculture were seldom the outcome of deliberate fraud. He expressed the hope that farmers would in the future avail themselves even more than in the past of the facilities provided by the new Act to have their fertilisers and feeding stuffs examined by the Official Agricultural Analysts, in order to ensure that their supplies were of the required standard, and that they were receiving value for their money.

Lord Atkin, in proposing the health of the Society, spoke of the value of the services of Public Analysts to the community, and contrasted the condition of the purity of food at the present time with that which was prevalent before the passing of the first Food and Drugs Act. He expressed the view that definite standards should be fixed for foods, and in particular for milk, and that the onus should be upon the vendor to prove that the article sold conformed to that standard.

The fact that vendors could defy the recognised standard for milk with an explanation about the idiosyncracies of the cow was due, not to legislation, but to a decision of three out of five judges in a certain criminal case. He had always longed for the time when an enterprising municipal authority would really fight this cause in a civil case, and take it, if necessary, through the Court of Appeal to the House of Lords, for the benefit of the community. It would bring great advantage to the public if that former decision could be altered. Lord Atkin also referred to the extension of the original basis of the Society, which now included the chemists of many of the leading industrial firms, and he laid stress upon the benefit to the community from the co-operation between these chemists and Public Analysts.

The PRESIDENT, replying to the toast, said that the income-tax authorities had recently defined a "learned society" as one that existed primarily for the benefit, not of its members, but of the public, and claimed that our Society, through the work it had done in helping to secure better food for the community, was entitled to that designation. The extension of its membership to include "other analytical chemists" gave it a still more authoritative position than formerly, for it could now speak as representing every branch of the profession.

The health of the Kindred Societies was proposed by Mr. A. CHASTON CHAPMAN, who pointed out how the various scientific societies, and particularly those connected with chemistry, were becoming more closely associated, owing to the way in which their work tended to overlap. Although he regarded this as a step in the right direction, he was personally of the opinion that each Society should retain its individual entity.

Sir F. GOWLAND HOPKINS, replying for the Kindred Societies, paid a tribute to the usefulness of the Journal of the Society of Public Analysts (THE ANALYST) to workers in biochemical laboratories.

Mr. E. HINKS proposed the health of the numerous guests, the toast being acknowledged by the LORD MAYOR OF NEWCASTLE and Mr. GEORGE GRAY.

Annual Report of Council

March, 1932

THE Roll of the Society stands at 668, an increase of 7 over the membership of last year.

The Council, with great regret, has had to report the deaths of:

J. Miller.
Gilbert John Alderton.
Meredith Wynter Blyth.
Shelton Gottlieb Agar.
George Craig.
Henry Droop Richmond.
Hubert Taylor.
William Foulkes Lowe.

H. Droop Richmond served several periods on the Council of the Society. He was a Past Vice-President, and occupied the position of Treasurer for two years. ("Obituary," ANALYST, 1931, **56**, 700.)

M. Wynter Blyth was a well-known Analyst, who took an active interest in the affairs of the Society, and was a Member of Council during 1906–1907. ("Obituary," ANALYST, 1931, **56**, 353.)

In W. Foulkes Lowe the Society loses an old member, whose membership dated from 1888. ("Obituary," ANALYST, 1932, **57**, 71.)

During the year, seven meetings of the Society were held, and the following papers were communicated:

"Some Factors Affecting the Solubility of Milk Powder." By L. H. Lampitt, D.Sc., F.I.C., and J. H. Bushill, M.Sc., A.I.C.

(i) "The Determination of the Hydroxyl Content of Organic Compounds: Estimation of Castor Oil." (ii) "The Determination of the Carbonyl and Aldehyde Content of Organic Compounds: Estimation of Phenylhydrazine." By S. Marks, M.Sc., A.I.C., and R. S. Morrell, Ph.D., F.I.C.

"Food Control in Holland." By A. van Raalte, D.Sc., and J. Straub.

"The Determination of Small Quantities of Methane." By H. R. Ambler, B.Sc., F.I.C.

"The Fatty Acids and Component Glycerides of Indian Ghee." By R. Bhattacharya and T. P. Hilditch, D.Sc., F.I.C.

"The Investigation of Japanese Beeswax." By H. Ikuta.

"The Denigès-Oliver Test for Morphine." By J. Bamford.

"Carbon Monoxide Poisoning: Its Detection and the Determination of the Percentage Saturation in Blood by means of the Hartridge Reversion Spectroscope." By R. C. Frederick, A.I.C.

"Experiments on the Hardness of Fats." By H. M. Mason, M.Sc., F.I.C., and G. Walsh, B.Sc., A.I.C.

"A New Process for the Determination of Small Amounts of Bromide in Chloride." By B. S. Evans, M.C., Ph.D., F.I.C.

"The Use of Bromine as a Reagent in the Determination of Alkaloids." By S. G. Walton and R. G. O'Brien.

"A Demonstration of a New Development in Filter Papers." By E. J. Guild.

"The 'Rope' Spore Content of Flour and its Significance." By A. J. Amos, B.Sc., A.I.C., and D. W. Kent-Jones, Ph.D., B.Sc., F.I.C.

*"The Separation of Tin from Tantalum and Niobium." By W. R. Schoeller, Ph.D., and H. W. Webb.

"A New Method for Detecting Decomposition Products in Anaesthetic Chloroform." By N. L. Allport, A.I.C.

"Contaminations in Morphine Deposited in the British Pharmacopoeia Process for the Analysis of Opium." By J. N. Rakshit, F.I.C.

"The Identification of Wood and Wood Charcoal Fragments." By J. Cecil Maby, B.Sc.

"The Examination of Dyed Leather in Cases of Alleged Dermatitis." By T. Callan, M.Sc., Ph.D., F.I.C., and N. Strafford, M.Sc., F.I.C.

"The Determination of Chlorides in Dairy Products and Biological Material." By W. L. Davies, M.Sc., Ph.D., F.I.C.

*"A Reliable Method for the Quantitative Separation of Titanium from Tantalum and Niobium." By W. R. Schoeller, Ph.D., and C. Jahn.

*"The Separation of the Earth Acids from Metals of the Hydrogen Sulphide Group." By E. F. Waterhouse and W. R. Schoeller, Ph.D.

"The Evaluation of the Menthone Content of Peppermint Oil." By J. Reilly, M.A., D.Sc., F.R.C.Sc.I., N. Noonan, M.Sc., and P. J. Drumm, Ph.D.

"The Determination of Vanillin in Chocolate and Cocoa Butter." By D. M. Freeland, A.I.C.

"The Direct Determination of Nitrogen in Gases." By H. R. Ambler, B.Sc., A.I.C.

"A Micro-Method for the Determination of Uronic Anhydride Groups in Pectic Substances." By H. W. Buston, Ph.D., D.I.C.

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* Work done under the Analytical Investigation Scheme.

"The Composition of Linseed Oil." By N. E. Cocchinaras, Ph.D.

"Oil from Malayan *Aleurites Montana* and the Properties of Hong Kong Oil." By T. Hedley Barry.

"The Calcium Fluoride Method for the Determination of Fluoride, with Special Reference to the Analysis of Nickel Plating Solutions." By S. G. Clarke, Ph.D., A.I.C., and W. N. Bradshaw, B.Sc.

The following papers were read at meetings of the North of England Section:

*"The Rapid Quantitative Determination of Solid Saturated Fatty Acids." By T. P. Hilditch, F.I.C., and J. Priestman, Ph.D.

"A New Method for the Determination of Solid Unsaturated Fatty Acids." By L. V. Cocks, F.I.C., B. C. Christian, Ph.D., A.I.C., and G. Harding, F.I.C.

"Some Aspects of the Bacteriological Examination of Water." By W. G. Carey, F.I.C.

"River Pollution Prevention Problems." By J. W. H. Johnson, M.Sc., F.I.C.

"Documentary Evidence in Criminal Trials." By C. Ainsworth Mitchell, M.A., D.Sc., F.I.C.

"The Analyst in the Witness-Box." By W. H. Roberts, M.Sc., F.I.C.

A considerable number of other original papers and notes also appeared in THE ANALYST.

The Editor of THE ANALYST, Dr. C. A. Mitchell, reports that the number of pages for the year is the largest in any volume of THE ANALYST so far published. The question of the paper on which THE ANALYST is printed has received the consideration of the Publication Committee. After expert advice, it was decided that the body of the Journal should consist of the same paper as at present, which conforms with the Library Association standard. Owing to the increased demand, the number of copies of THE ANALYST printed was increased at the commencement of the year.

The Honorary Treasurer's statement has been published separately; it shows that under his careful supervision expenses have been successfully met, and that the Society is in a sound financial position.

The Council records its appreciation of the facilities which have been readily afforded to the Society by the Chemical Society and by the Institute of Chemistry in providing accommodation for Committees.

The Standing Committee on Uniformity of Analytical Methods and its Sub-Committees have continued their work, and, though only one finished report has been received during the year, there are several reports nearing completion. The report received, which was the eighth of the series issued by the Essential Oils Sub-Committee, contained recommendations with regard to the determination of cineole in essential oils other than cajuput and eucalyptus oils. A new Sub-Committee has been formed, consisting of representatives of the Society and of interested industrial organisations, under the chairmanship of Professor T. P. Hilditch, D.Sc., F.I.C., to consider the determination of unsaponifiable matter in oils and of unsaponified fats in soaps. The duties of Honorary Secretary of this Sub-Committee have been undertaken by L. V. Cocks, F.I.C. Again the Council expresses its appreciation of the work of the Chairman, E. Hinks, B.Sc., F.I.C., and the members of the Standing Committee, and also of the Chairmen and members of its Sub-Committees. It fully realises the large volume of work entailed by the investigations which have been undertaken.

The Council concurred with the report issued by the "Ad Hoc Committee" appointed by the British Chemical Standardising Body, to explore the possibilities of chemical standardisation. The British Engineering Standards Association has now become the British Standards Institution, and its work is divided into

Sections, one of which is termed "The Chemical Division." The Council has elected E. R. Bolton, F.I.C., to serve as its representative on this division.

During the year, the Ministry of Health set up a Departmental Committee "to enquire into the working of the law as to the composition and description of articles of food other than milk, and to report what alterations, if any, in the law, or its administration, appeared to be desirable." A request was received to hear evidence from the Society, and the Council appointed the President (J. T. Dunn, D.Sc., F.I.C.), E. Hinks, B.Sc., F.I.C., and F. W. F. Arnaud, F.I.C., to represent the Society. The Council of the Society submitted a memorandum of the evidence which it proposed to give, but before the witnesses could be heard, owing to the financial situation of the country demanding measures of economy, the work undertaken by this Committee was suspended. The Council regrets this, while expressing its hope that at the earliest possible moment the enquiry will be re-opened by the Ministry. It is to be noted that, in the terms of reference, milk is excluded from consideration by the Departmental Committee. The Council views with concern the movement that is noticeable in many quarters for the repeal of the Sale of Milk Regulations, and also the character of the legislation which is advocated in this connection. The Council is carefully watching the matter, and will take advantage of every opportunity afforded to put forward the views of the Society.

For many years the Editor, C. A. Mitchell, D.Sc., F.I.C., has represented the Society on the Chemical Society Library Committee. Under the rules of the Chemical Society he must now retire from the Committee. The President and Council have expressed to him their warm appreciation of his services.

The Food Manufacturers' Federation invited the Society to suggest a standard for added flour in shredded suet. A meeting with representative manufacturers of shredded suet took place, and the view of manufacturers was ascertained. The Council considered that the amount of added starch would best be limited by prescribing a minimum content of fat in the shredded suet. It also recommended that this minimum be 83 per cent., and stipulated that any addition to suet should be declared. (*See* ANALYST, **1931**, **56**, **778**.)

The question of jam standards again received the attention of the Public Analysts' Committee, and further views with regard to these have been published from time to time. (*See* ANALYST, **1931**, **56**, **391**, **701**.)

Besides the investigations which were completed during the year under the Analytical Investigation Scheme, there are at present six investigations proceeding. The Secretary would at all times welcome further suggestions for work under the Scheme.

The North of England Section shows continued activity, and, at its last General Meeting, it was stated that five meetings had been held during the year. A Summer Meeting, held at Scarborough, was largely attended by Members of the Section, and a few Members from the South were also present. At this meeting the Chairman—C. J. H. Stock, B.Sc., F.I.C.—moved a resolution, which was unanimously carried; expressing the devotion of the North of England Section to the aims and interests of the parent body. (*See* ANALYST, **1931**, **56**, **497**.)

J. T. DUNN, *President*.
F. W. F. ARNAUD, *Honorary Secretary*.

Annual Address of the President

(DR. J. T. DUNN, F.I.C.)

(Delivered at the Annual General Meeting, held on March 4, 1932)

LADIES AND GENTLEMEN,

At the end of another Session we can still congratulate ourselves on being in vigorous life and on increasing our membership and our usefulness. Though we have to lament the removal by death during the year of eight of our members (one of whom, William Foulkes Lowe, had been a member for forty-three years, and another, Henry Droop Richmond, for forty-one), yet our roll of membership holds seven more names than it did at our last Annual Meeting. The number of papers read at our meetings and communicated to our Journal shows no tendency to diminish (indeed, the Editor's difficulty is rather how to accommodate them all, having regard to the desirability of keeping successive monthly issues approximately uniform in size); and a perusal of their titles, as enumerated in the Council's report, will make manifest their variety and the wide extent of ground which they cover. The value and usefulness of our journal are shown by the growing demand for it outside of our own membership—a demand so great that we have had to increase the number of copies that we print. Thanks to the vigilance and care of our Honorary Treasurer, our expenditure has been kept within our income, and we are financially in a position which many kindred Societies would in these difficult times consider enviable.

Our North of England Section continues its vigorous career, and its loyalty to the parent Society is on a par with its activity. It has furnished us with several new members during the year, and has added its contributions to THE ANALYST. It has continued the practice of including in the programme of its meetings, whenever possible, visits to works and manufactories, and it had again last year a Summer Meeting at Scarborough, equally successful with the former one on its serious side, and much more successful in the number of members who attended it, among whom, it is pleasant to remember, were several from the southern portion of the Island. Both the works visits and the Summer Meeting afford opportunities for personal intercourse among the members that are not possible to anything like the same degree during the more formal portions of the meetings, and that do a great deal to foster and develop among them the spirit of comradeship and of loyalty to the Society.

It is pleasant to be able to congratulate our veteran member, Dr. Dyer (and it is also a matter on which the Society is to be congratulated), on the completion of a task which, though it may have been laborious, and at times have given rise to sad and regretful memories, must, on the whole, I think, have been a labour of love and a very pleasant occupation. His "Reminiscences of the First Fifty Years" of our Society is now in paged proof, and we have now only to wait for the completion of Dr. Mitchell's complement to it—"A Review of its Activities." Dr.

Dyer's qualifications for undertaking this work are, of course, unique. We are all under a deep debt of gratitude to him, and it is very pleasant to think that he is still possessed of such health and vigour that he has been able, not only to complete his history, but to come down with regularity to our meetings, and give us the pleasure of his presence and the advantage of his counsel. As one who has had the privilege of reading Dr. Dyer's work in proof, I can say with certainty that when you do read it you will not only unanimously wish, as I know you all do now, that he may long be spared to continue his active association with us, but will regret the improbability that he may be able, when the Society celebrates its centenary, to give us the history of its second fifty years also.

The Society of Chemical Industry, at its December Council meeting, decided to form a "Food Group" in the Society, for those of its members who are mainly interested in the technology of food products, much on the lines of the Chemical Engineering Group, which has existed in the Society for some considerable time. It was recognised that, as our Society deals very largely with the analysis of foods, it was desirable to avoid any overlapping or possible clashing of interests, and to secure, if possible, some measure, not only of co-ordination, but of co-operation; though, as the purview of the members of the Food Group would cover the technological and industrial aspects of food manufacture, rather than the analysis of food products, serious overlapping was not greatly to be feared. Representation of this Society on the Committee of the Food Group was thought to be desirable, but the constitution of the Group as a body of members of the Society of Chemical Industry prevented this. The difficulty was got over, however, by giving the Committee of the Food Group power to co-opt an additional consultative member from outside; and our Treasurer, Mr. Hughes, was so co-opted, and sits on the Committee to form a link between the Group and this Society. There is no reason to think that the procedure of the Food Group will be in any way detrimental to the work or the interests of this Society, and we may heartily welcome its formation and wish it success. The Group is holding its inaugural meeting, jointly with the London Section of the Society of Chemical Industry, in these rooms, on Monday next at eight o'clock, when Dr. Lampitt will give an address on "Science and Food."

Four of last year's papers were accounts of work done under the Analytical Investigation Scheme. This scheme was suggested, I believe, by Mr Chaston Chapman, about 1901. It was referred to in his presidential address, in 1904, by Mr. Fairley, who then said that several investigations were in progress under its auspices. In February, 1908, attention was drawn to the Scheme by publication of its objects and methods of work in THE ANALYST; and Mr. Chapman, in his presidential address of 1915, mentioned that up to that time the results of thirty-seven investigations under the Scheme had been presented to the Society. I mention the Scheme now because one long and important investigation under it has just been brought to practical completion. We may, I think, congratulate Dr. Schoeller and his colleagues on their work. They took up with great courage a piece of work which most chemists would have thought very unpromising, perhaps very uninteresting, and have pursued it with great patience and perseverance over a period of more than ten years; as a result, they have established accurate and workable methods for the determination of tantalum and columbium, and for their separation from one another, and from tin, titanium, tungsten, hafnium, and zirconium. This work is described in a series of twenty-one papers (one read after the date of Council's Report), all but the first two of which have appeared in THE ANALYST, as results of work undertaken under the Analytical Investigation Scheme.

Of late years the Scheme has to its credit, besides the work of Schoeller and his associates, that of Nicholson and Rhind, Price, Hooper, Fear and A. E. Jones on tannins, and of Hilditch and Priestman on the separation of solid and liquid fatty acids; and there are at present six other investigations proceeding under the Scheme. The work already completed, and that still going on, shows that the Scheme has amply justified its existence; but one could wish that the opportunities it affords for bringing into relation with one another those who have need of trustworthy analytical processes for particular ends, or wish to have the accuracy and trustworthiness of published methods inquired into, on the one hand, and those who have time and opportunity for investigation, and are looking for appropriate objects of inquiry, on the other, were still more widely taken advantage of.

The work of the Analytical Investigation Scheme naturally calls to mind that of the Standing Committee on Uniformity of Analytical Methods. Many may think that the output of this Committee is small, and its work very slow. But, in the nature of things, the analytical processes which the Committee, through its Sub-Committees, is called upon to examine and report upon, are almost all of them, necessarily, processes of difficulty and uncertainty at their present stage, and involve, in overcoming those difficulties, a very large amount of work. This work, too, is, for the most part, team work, and has to be carried out by teams that can only devote a part—sometimes a very small part—of their time to it; teams, too, the members of which are often widely separated geographically, so that collation of results and consultation among the members necessarily take much time. The reports furnished by the Sub-Committees and published in THE ANALYST, give only a faint indication of the amount of labour involved in their preparation. To the members of the Sub-Committees, and, in many instances, to the firms under whom the members work, and who have supplied materials and helped in other ways, not the Council alone, but the whole of the members of the Society, are grateful, and more especially those members who, through the labours of one or other of the Sub-Committees, are furnished with a definite and workable method of analysis for their daily routine, enabling them to reach results comparable with those of other workers, where formerly discrepancy and confusion were only too frequent.

Work, generally similar to that of the Committee on Uniformity of Methods of Analysis, will in future be carried out under the auspices of the new Standards Institution. The recommendations of the Committee appointed by the Conference on Standards of June, 1930, to which I referred a year ago, have been carried into effect; the British Engineering Standards Association has been widened in its scope, and has become the British Standards Institution. It is to work through four divisions, concerned respectively with Engineering, Chemistry, the Building Trades, and the Textile Trades. Each division is controlled by a

Council—that of the Chemical Division consists of thirty-six members, twenty-eight of whom represent various Societies or organisations, of which our Society is one, and the other eight, to be co-opted, will be persons whose services are likely to be of special aid to the Council. The General Council of the Institution consists of forty-one members, nine elected by each of the four Divisions, and one each from the Institution of Civil Engineers, the Board of Trade, the Department of Scientific and Industrial Research, the Federation of British Industries, and the Association of British Chambers of Commerce. The General Council will decide the broad policy of the Institution, and deal with matters of general interest; but, subject to being in accord with that broad policy, each divisional Council will manage its own business without any control or interference from outside. The Divisional Councils are now organising themselves for work, and, in the capable hands of Mr. Bolton, we may be quite sure that the representation of this Society is safe. It may interest members to know that the Joint Committee for the Standardisation of British Chemical Glassware, on which this Society was represented, but the administration of which was conducted through the Institute of Chemistry, has turned over the continuation of its work to the new body.

The Council welcomed the appointment by the Ministry of Health of the Committee to inquire into the working of the Food Laws, and gladly embraced the opportunity of giving evidence before the Committee, in the hope that the Committee's deliberations would result in the removal of anomalies and objectionable features that exist in the present Acts, and in the introduction of greatly-needed reforms. Unfortunately, the sudden recognition of the need for drastic economies in the national expenditure caused the suspension of the Committee; and only a day or two before its first meeting, to which the Society's representatives had been summoned, we had notice that the meeting would not be held, and, shortly afterwards, further notice that the sittings of the Committee would be indefinitely postponed. We can only wait for the restoration of financial stability and the return of some measure of prosperity in the country, and hope that when that is achieved this matter will again receive attention at the hands of the Government of the time; for the urgency of reform will certainly be no less then than now, and most of the desirable alterations in the law will involve little or no cost to carry out.

The first point which we proposed to urge upon the Committee was the need for prescribed standards or limits of composition of articles of food, the prevention of misdescription, and the institution of a Statutory Advisory Committee to devise and recommend such standards or limits, and revise them or add to them from time to time as might become necessary. These matters, of standards or limits, and of a body which should ascertain and prescribe them, have for long been a matter of discussion, and the balance of opinion, at least among Public Analysts, has been overwhelmingly in favour of their introduction. Dr. Dyer tells us that at the first meeting of the Society in 1874 suggestions for standards or limits for certain articles of food were put forward, and referred to the Council for guidance, and I find that at a Conference on Food Adulteration, held at the International Health Exhibition in 1884—nearly fifty years ago—the matter was discussed. Dr. Bell, at that time head of the Somerset House laboratory, deprecated their wide introduction, on what would now seem, to most of us, the rather curious ground that it might tend to discourage the production and diminish the supply of any article of food; but Dr. Muter went wholeheartedly for it, and declared that there ought to be a permanent Commission appointed by law, consisting of three chemists, nominated respectively by the Government, by the Society of Public Analysts, and by the Chambers of Commerce, to examine all articles of food, and lay down limits. In 1893, in consequence of a Bill promulgated by Dr. Cameron to amend the Food and Drugs laws, which contained some objectionable clauses (but which was afterwards withdrawn), this Society called a conference to discuss the general question. At this conference a proposal was made that there should be constituted a chemical department of the Local Government Board, with which the Public Analysts, as officers of the Board, should be placed in direct relation. Consultation with this Department would, in effect, it was thought, result in the fixing of limits. Possibly as the result of this conference, or of the public attention which the conference attracted, a Select Committee was this year appointed to inquire into the working of the Acts, and the Society, for the consideration of the Committee, formulated a draft bill, which suggested, among other things, the creation of a Board of Reference, to consist of the Chief Chemical Officer of the Inland Revenue Laboratory, a nominee of the General Medical Council, three nominees (all to be Public Analysts) of the Local Government Board, and one nominee of the Board of Agriculture, who were to examine and report on the composition of various articles of food and drugs, describe, investigate, and advise regarding new or improved methods for their examination, set forth definitions and exceptions, and fix limits and standards of quality and purity. They were to meet from time to time, to issue new or revise old limits or standards. The Committee, in its report, adopted many of the suggestions of the Society, but the resultant legislation, which was not effected till 1899, contained no reference to standards or limits, nor to an advisory or prescribing body. Meanwhile, successive Presidents, in their addresses, referred to the matter. Sir Charles Cameron, in 1895, said: "Every effort should be made to induce the Committee to recommend the fixing of standards for all articles that admit it"; and Dr. Stevenson, in 1896: "Our earnest endeavour in the near future must be to secure limits below which articles of food and drugs must not be allowed to fall; limits fixed by some competent and authoritative body, on which Public Analysts must, of course, be adequately represented."

So far as colouring matters and preservatives are concerned, the Departmental Committee on Preservatives of 1901 expressed the same view; they recommended "That means be provided, either by the establishment of a separate court of reference or by the imposition of a more direct obligation on the Local Government Board, to exercise supervision over the use of preservatives and colouring matters in foods"; and the Royal Commission on Arsenical Poisoning of 1903 was still more definite in its proposals, its report reading: "We consider that the Local Government Board (under advice as indicated in this report) should be the authority to prescribe, and from time to time to vary, standards for the purposes of the Food and Drugs Acts. Obviously, account would need to be taken of sundry medical, physiological, chemical, and administrative questions in fixing such standards . . . and manufacturers should be fairly dealt with. The Committee on Food Products Adulteration (1893), and, more recently, the Committee on Preservatives, alike came to the conclusion that food standards in certain instances were essential to efficient administration. Both Committees realised the impossibility of satisfactory standards being fixed by the central authority in the absence of full preliminary inquiry, and they recommended the establishment of a Board (Court, Permanent Commission or Standing Committee) of Reference, which should consist of a small number of scientific men, nominated by the Crown or departmentally, as the authority to advise on points arising in connection with the Sale of Food and Drugs Acts, and to prescribe the standards which should be fixed for the purposes of those Acts. We are of opinion that if a Government Department, the Local Government Board, or the Board of Agriculture, is to impose standards for the purposes of the Food and Drugs Acts, it is essential that its action should be based upon the advice of a scientific body of this nature."

Mr. Fairley, in his 1905 address, spoke strongly on the matter, quoting the words of the Council in 1897 as being still applicable to the situation, and Mr. Tatlock, in his presidential address in 1909, again referred to the matter, and expressed the hope that it might be made the subject of discussion at a "field-night" of the Society.

In 1913 Mr. John Burns introduced a Bill, which, among other provisions, proposed to give power to the Local Government Board, "after such inquiry as they may think necessary," to make regulations defining an article of food in any matter affecting its nature, substance, or quality. To place such a power in the hands of the Local Government Board, with no further assurance that interested and qualified opinion would first have been obtained than "after such inquiry as the Board may think necessary," would hardly have satisfied our Society, and probably would still less have satisfied the manufacturers of, and dealers in, articles of food; it was, in fact, very strongly deprecated by Mr. Archbutt in his address in 1914, in which he urged the need of defining clearly the machinery by which such regulations were to be made; but the Bill was withdrawn, and the necessity for opposing or modifying its proposals disappeared.

No further step was taken till the Food and Drugs Act of 1928 was passed, which, as we all know, was only a consolidating Act, and introduced no new features; especially was there no part of it dealing in any way with the general setting up of standards or limits of composition. In 1929 our Society addressed a letter to the Committee of Civil Research, pointing out the difficulties which frequently arise in the administration of the Food and Drugs Acts, showing that many of these difficulties would be overcome if there were recognised standards of composition for a variety of foods, and urging the desirability of appointing a body to examine into the necessity for this, and the provision of a scheme to make funds available for the cost of investigations that might be involved.

In our memorandum for the Committee of last year we brought all this forward, and laid stress on the unanimity of qualified opinion on the point coming from so many different sources; and we shall, I hope, urge the matter no less strenuously when the opportunity for so doing arrives. It would serve no good purpose, and would take more time than we have at our disposal, to go over *seriatim* the whole of the points which we were prepared to urge upon the Committee, but I thought a brief summary of the history of opinion upon this important matter of "Standards and how to fix them," would, perhaps, be interesting and useful.

Now, ladies and gentlemen, this is the last occasion on which I shall occupy this chair, save for a few moments when I come down in April to hand over the position to my successor. I have endeavoured to carry out the President's duties to the best of my ability, but I claim no credit or virtue on that ground, for the work, and all that it has involved, have been a source of unmixed pleasure and enjoyment to me. I am glad to think that I leave the Society in at least as flourishing a condition as when I took over the chair; but neither do I claim any credit for that—for I have had the help and guidance of a Council and officers devoted to their work, assiduous in their attendance at meetings, and so varied in their attainments and their special directions of thought, that the very best advice and counsel has been at my disposal in every contingency. I name none of them, for I should have to name them all; and I am grateful, not only for their work as officers and members of Council, but for their unbroken kindness to me, and for the pleasure which personal intercourse with them has been to me.

I have attended every meeting of the Society since you elected me. I wish I could continue to attend every meeting in the future, but I recognise that that is an ideal to which I can hardly hope to attain. I leave the chair with none but happy memories, and have but one regret, which is, that the pleasant personal intercourse with my fellow-members cannot continue except to a diminished extent. There is, I think—I have said it to the Northern Section, and I say it here again—something in this Society, a spirit of some sort, which inspires its members with affection for the Society to an extent greater than I find in any similar Society that I know. I do not seek to define it or explain it: I am content to feel it and know that it exists. Long may it continue: and as long as it does continue, presidents may come and presidents may go—but the Society of Public Analysts and other Analytical Chemists will go on for ever.

A Micro-Method for the Determination of Uronic Anhydride Groups in Pectic Substances

By HAROLD WILLIAM BUSTON, PH.D., D.I.C.

(*Read at the Meeting, December* 2, 1931)

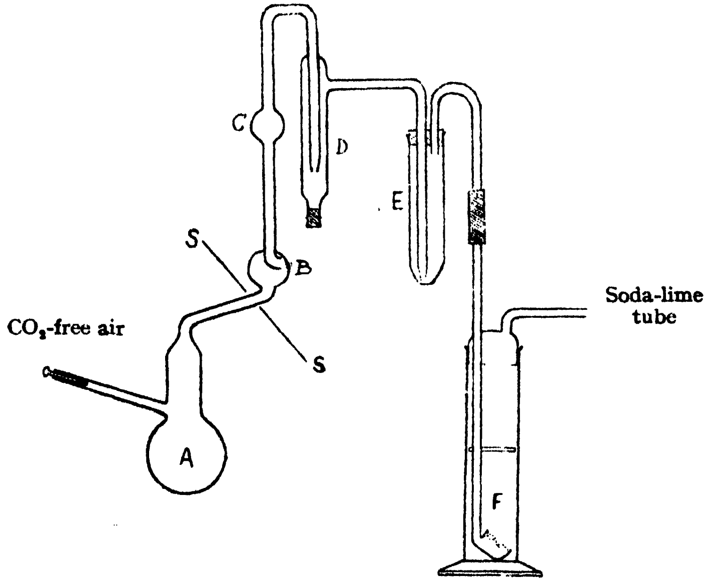
SINCE the pectin molecule was shown by Nanji, Paton and Ling (1925) to be based upon a combination of sugar residues and residues of "uronic acids," the determination of the "uronic anhydride" content of pectic substances has become part of the regular technique. The method devised by these workers for the determination, and subsequently generally adopted, was based on the observation that, on distillation with 12 per cent. hydrochloric acid, the uronic anhydride residues yield carbon dioxide quantitatively, according to the equation:

$$\underset{\text{uronic anhydride residue.}}{-C_6H_8O_6-} = \underset{\text{furfural.}}{C_5H_4O_2} + 2H_2O + CO_2.$$

The determination thus involved the estimation of the carbon dioxide produced under certain given conditions. When dealing with a substance such as calcium pectate, which is regarded as having a definite composition, the results obtained were only approximately equal to those calculated from the accepted formula. The error lay chiefly in the titration of the standard barium hydroxide, in which the carbon dioxide was absorbed. Working with the type of apparatus most frequently used, three absorption towers in series are found necessary to trap all the carbon dioxide; each tower contains 100 c.c. of *N*/20 barium hydroxide, of which 20 c.c. samples are withdrawn at the end of the operation, and titrated. Thus a small titration error may be magnified considerably in calculating the result. Apart from this drawback, the apparatus necessary is very cumbrous, large amounts of reagents are required, and the determination, which involves 3 hours' distillation, takes a considerable time to carry out. This seemed a case, therefore, where the use of a micro-method could be adopted with advantage. The familiar advantages of micro-methods—the use of much smaller amounts of material and reagents, and the curtailing of the time involved—were enhanced by the fact that it was found possible to use only one absorption tower, and thus to reduce the error arising from inaccurate titration.

APPARATUS.—The preliminary experiments were carried out with the micro-Zeisel apparatus described by Pregl (1924). Some difficulties were met with in using this apparatus, but the early results obtained gave sufficient promise to lead to a continuation of the experiments.

A modified form of the micro-Zeisel apparatus was designed, and is shown in the diagram. The bulb (A) in which hydrolysis of the pectin takes place has a capacity of about 8 c.c.; the vertical tube which serves as a reflux condenser is displaced some 3 cm. to the right, so that it is removed from the column of heated air rising from the bulb. Thus the refluxing process is made more efficient, and is further improved by placing a screen (SS) of asbestos paper slantwise across the tube below the bulb (B), and keeping the lower part of this tube cool by means of a moistened filter paper. The bulb (B) serves to prevent loss of material in the event of the liquid in A bumping during the hydrolysis, while the upper bulb (C) breaks the column of liquid which tends to collect in the tube, and prevents any liquid from being carried over into D. The length of the vertical tube (reflux) is 15 cm., and the two bulbs have a diameter of about 1 cm. The trap (D) is empty, but has a loose plug of cotton-wool at the entrance to the side tube. The bubbler (E) contains a few drops of saturated silver sulphate solution, into which the delivery tube just dips; above this, the tube is packed for a distance of 2–3 cm. with glass wool, soaked in a paste of silver sulphate. Thus the gases passing through are brought thoroughly into contact with silver sulphate, without the use of relatively large amounts of water in which carbon dioxide might be retained. A plug of cotton wool in the upper part of E prevents any spray of silver sulphate from being carried over into the absorption tower.



The gas tower (F), which contains the barium hydroxide, is one of a pattern now standardised by Messrs. Schott of Jena. It has a capacity of 20 c.c., and the delivery tube is closed with a disc of sintered glass, of a coarse grade of porosity, which breaks up the passing gas into a fine mist of bubbles. It was the use of this type of bubbler that enabled absorption to be carried out in the one tower. When the gas is passing, some amount of splashing takes place up the sides of the tower; this is minimised by fitting a disc of rubber across the tower, just above the surface of the liquid, as indicated in the diagram. A soda-lime guard-tube closes the exit from the absorption tower. The whole apparatus was designed to have the smallest internal volume practicable, in order to facilitate thorough removal of carbon dioxide by the current of air.

METHOD.—In carrying out the determination, a current of air is passed through the apparatus during the experiment. This is supplied most conveniently from a small cylinder of compressed air, with a finely adjustable valve. In the experiments quoted below, the air taken into the compressor was passed through caustic soda; any carbon dioxide escaping absorption at this stage was removed by passing the air from the cylinder first through 10 per cent. caustic soda solution, using a delivery tube with a sintered glass disc of the same type described above, and then through a short soda-lime tube. The air is passed at a rate of about 4 c.c. per minute. Four c.c. of 13 per cent. HCl, 90 per cent. saturated with sodium chloride, are placed in the bulb A, and the substance under examination (6–10 mgrm.), weighed out into a small cup of thin tinfoil (see Pregl, *loc. cit.*), is introduced through the side tube. [The use of the HCl–NaCl mixture follows the recommendation of Kullgren and Tydén,* who used a saturated solution of sodium chloride in 13·15 per cent. hydrochloric acid for furfural distillations; it was found that this mixture bumped severely during the heating, but this could be avoided by using a little less sodium chloride.] In the opening of the side tube rests a loosely-fitting glass pin, as in the micro-Zeisel apparatus. The absorption tower is charged with 10 c.c. of *N*/50 barium hydroxide solution, measured out by means of an automatic pipette.

After air has been passed through the apparatus for a few minutes, the tower F is connected, and the acid in A gently boiled over a micro-burner; a few chips of quartz in A promote smooth boiling. In 10–15 minutes, barium carbonate begins to appear in F. The amount rapidly increases at first, but the distillation is continued for 60–70 minutes, since experiment has shown that the process is virtually complete in this time (see below). If the boiling is gentle, no acid escapes into D, the refluxing being quite efficient. At the end of the distillation, F is disconnected, closed with a rubber stopper, the contents mixed, and the barium carbonate allowed to settle. Five c.c. of the liquid are withdrawn by means of an Ostwald pipette, having a rubber bulb attached, and titrated with standard *N*/100 oxalic acid, phenolphthalein being used as indicator.

Before carrying out any estimations, tests were made to examine any possible sources of error, and "blanks" performed. No indication was found that the air used introduced any carbon dioxide, nor that any acid was carried over into the absorption tower. The completeness of absorption of carbon dioxide in the tower was also carefully tested. The pipettes and micro-burette used were accurately calibrated, and the normality of the barium hydroxide and oxalic acid checked from time to time.

The accompanying table summarises the results of a number of determinations of uronic anhydride content of samples of pectic substances. The results obtained indicated that the micro-method is capable of giving results of the same order of accuracy as the macro-method.

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* "Über die Bestimmung der Pentosanen," *Ing. Vetenskaps. Akad. Stockholm*, 1929, Handl. 94, p. 19.

TABLE I

Substance.	Time of distillation (minutes)	Percentage of uronic anhydride:		
		Micro-method	Macro-method	Calc. from formula
Calcium pectate ($C_{35}H_{46}O_{33}Ca_2$) Sample I	30	42·88		65·54
	50	·60·28; 61·32		
	60	62·92; 63·08		
	70	64·12		
	100	64·56	63·43*	
Sample II	70	65·98	—	
Sodium pectate ($C_{35}H_{46}O_{33}Na_4$)	70	65·76	66·50*	64·80
Pectin (methoxyl = 8·2 per cent.)	60	66·85	—	67·66†

* Time of distillation, 180 min.

† Calculated for tri-methoxy pectic acid, $-OCH_3$ = 8·98 per cent.

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Nanji, Paton and Ling, *J. Soc. Chem. Ind.*, 1925, **44**, 253T.
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DISCUSSION

Dr. H. E. Cox enquired whether there were any other sugars which yielded carbon dioxide on oxidation by the method, and whether in the case of jam it was necessary as a preliminary to isolate pure calcium pectate, or could the process be carried out on the more or less crude pectin? What relationship existed between the uronic anhydride groups and furfural?

Mr. T. RENDLE asked if the author could say whether the volume of carbon dioxide varied with pectin from different fruits. The method would probably be very useful if this were the case. He would also like to know if all pectinous bodies were "pectin," so far as this test was concerned.

Dr. BUSTON, replying, said that the sugars themselves did not yield carbon dioxide under the conditions of the experiment, but in natural fruit juices, etc., the pectins were always associated with substances of the hemicellulose type. The method was designed to assist in the investigation of the constitution of pectic substances and hemicelluloses themselves, and its application to the analysis of jams was not contemplated. It was generally accepted that the furfural yield from such groups approximated 16·7 per cent.

The amount of carbon dioxide obtained from the pectins of different fruits would vary with the degree of esterification of the pectic acid present, and also with the amount of contaminating hemicellulose. For pure pectic substances the carbon dioxide yield lay between 17·64 per cent. (for pectic acid) and 16·9 per cent. (tetra-methyl ester), irrespective of the source from which the pectin was prepared.

ADDENDUM.—I am indebted to Mr. Bacharach for the suggestion that the use of achromatic indicators, such as those described by Lester Smith (*Quart. J. Pharm.*, 1930, **3**, 499), would render the end-point in micro-titrations sharper. Opportunity has not been found to examine the matter in detail, but preliminary tests indicate that with a mixed methyl red- methylene blue- phenolphthalein indicator (2:1:100) a very satisfactory end-point is in fact obtained. It is surprising that achromatic indicators have not been more widely used in micro-titrations, where they offer considerable advantages.

Mohler's Test for Benzoic Acid

By EDWARD T. ILLING, B.Sc., F.I.C.

PART I

AN INVESTIGATION OF GROSSFELD'S MODIFICATION OF THE TEST

MOHLER's test does not appear to have given satisfactory results in the hands of many workers; but, as fatty acids in moderate amount do not interfere with the production of the colour, due to *m*-diamino-benzoic acid, it was thought that a little study might well be devoted to the essential points.

Grossfeld's modified test is as follows:*—"The residue of benzoic acid is heated for 20 minutes in a steam-bath with 1 c.c. of concentrated sulphuric acid and 0·1 grm. of potassium nitrate. The mixture is cooled, 2 c.c. of water added, cooled again, and treated with 10 c.c. of 15 per cent. ammonia solution and 2 c.c. of 2 per cent. hydroxylamine hydrochloride solution. The colour develops slowly. It may be hastened by warming on the steam-bath, but attains its maximum on subsequent cooling. It may be matched with a solution of 0·86 grm. of ammonium iron alum in 1 litre of water, added to a 2 per cent. solution of potassium thiocyanate in the following amounts." The amounts of iron alum solution equivalent to varying quantities of benzoic acid are given.

Tests carried out by this method gave very inconsistent results. The essential details for success do not appear to have been worked out. The following points are worthy of notice, as bearing upon the quantitative aspect of the test:

(1) NITRATION.—This must be carried out under specific conditions. Temperature and time are important factors, as is also the quantity of sulphuric acid.

The best results were obtained by the use of a boiling tube immersed in boiling water for 20 minutes; but continuation of the nitration for a further 5 minutes has no effect upon the final result. It is obvious that if the nitration is carried out in a beaker either on a steam-bath, or even immersed in boiling water, the temperature throughout the liquid is not as uniform as it is when the containing vessel is a comparatively narrow tube immersed in boiling water. It is better to add first the potassium nitrate, and then the concentrated sulphuric acid.

(2) REDUCTION.—The reduction of the *m*-dinitro-benzoic acid must also be carried out under strictly standard conditions. The two essential conditions are again temperature and time.

The temperature must be carefully regulated, as the amino-compound is decomposed if it is heated at too high a temperature.

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* Ministry of Health Reports on Public Health and Medical Subjects, No. 39, January, 1927, by G. Monier-Williams, p. 33.

It was found that the amino-compound showed signs of decomposition (the reddish-brown colour was diminished and a yellow colour began to develop) when heated for 20 minutes at 70° C., but decomposition could not be detected when the duration of the heating was from 3 to 10 minutes. At a temperature appreciably below 60° C. (about 55° C.), the reduction was not complete in 20 minutes, but at 65° C. only 5 minutes were required for the maximum development of colour. The desired conditions are, therefore, 5 minutes at 65° C. A variation of 3 to 4 degrees either way during the heating has no appreciable effect. It should be noted that the temperature of the water in a beaker may fall about 5 to 10 degrees on introducing 6 to 8 tubes, so that it is advisable to have the water at about 72° C. at the beginning of the reduction.

(3) REACTION BETWEEN FERRIC IRON AND POTASSIUM THIOCYANATE.—The reaction between ferric iron and potassium thiocyanate is a reversible one, and, as neither of the reacting ions is coloured, the non-ionised ferric thiocyanate is evidently responsible for the colour. It is, therefore, apparent that the quantity of thiocyanate used is as important as that of the ferric iron solution. The colour is intensified by the increased concentration of either.

A solution of ammonium iron alum containing 1 grm., instead of 0·86 grm., per litre, has been used throughout these tests.

METHOD.—The method is as follows:—The benzoic acid residue (as the sodium salt*) is introduced into a boiling tube (6″ × ¾″), and the tube is heated in a beaker of boiling *brine* until the liquid is driven off, and all the drops of condensation water have disappeared. It is cooled, and 0·1 grm. of potassium nitrate and 1 c.c. of concentrated sulphuric acid are added. The tube is placed in boiling *water* for 20 minutes, then cooled, and 2 c.c. of water are added. The tube is held under running water, and 10 c.c. of 15 per cent. ammonia solution are *carefully* added, followed by 2 c.c. of a 2 per cent. hydroxylamine hydrochloride solution, and the contents are well mixed. It is next placed in a beaker of water at 65° C. for 5 to 6 minutes, then cooled, and the colour matched with that developed by mixing the amounts of iron ammonium alum and potassium thiocyanate solutions given below for varying quantities of benzoic acid.

Benzoic acid	Iron ammonium alum solution (1 grm. per litre)	Potassium thiocyanate solution (2 per cent.)	Volume made up to
Mgrms.	c.c.	c.c.	c.c.
0·1	0·2	0·2	15
0·25	0·3	0·3	15
0·5	0·5	0·5	15
0·75	0·7	0·6	15
1·0	1·0	0·8	15
2·0	1·5	1·5	15
3·0	2·0	1·5	15
4·0	2·0	2·3	15
5·0	3·0	2·5	15
6·0	4·0	3·5	50
7·0	4·0	4·5	50
8·0	4·5	3·5	50
9·0	5·0	4·0	50
10·0	5·5	5·5	50

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* Ammonium benzoate is volatile at 100° C.

The standards of 15 c.c. volume were made up in a graduated cylinder by adding the requisite amounts of the two constituents, and making up to 15 c.c., which is the volume of the solution obtained at the completion of the test. The colours were matched in 50 c.c. Nessler tubes. For 6 mgrms. or more of benzoic acid it is better to dilute to 50 c.c. and to use 100 c.c. Nessler tubes. These standards cannot be diluted, as the colours are not proportional in other dilutions.

The above test will detect 0·025 mgrm. of benzoic acid, and amounts of this acid differing by 0·025 mgrm. can be distinguished when working with 0·1 mgrm. or less, but with increasing depth of colour in more concentrated solutions of benzoic acid the sensitiveness of the test decreases.

Salicylic acid, phenolphthalein, saccharin, and vanillin all give yellow colours only. Fatty acids give no colour at all.

Cinnamic acid, when treated by the above process, gives a brownish colour, which can be distinguished from that given by benzoic acid. The test will detect 0·5 mgrm. of the acid, which represents 25 parts per million when working with 20 grms. of food, and thus in the presence of cinnamic acid the amount of benzoic acid indicated would be high. A mixture of 0·5 mgrm. of cinnamic acid and 0·5 mgrm. of benzoic acid gave a colour equal to that given by 1·5 mgrm. of benzoic acid. This quantity of cinnamic acid would have a very slight effect on the determination of the amounts of benzoic acid generally found in 20 grms. of food.

The depth of colour given by a mixture of 3·5 mgrms. of benzoic acid and 0·5 mgrm. of cinnamic acid could hardly be distinguished from that given by 3·5 mgrms. of the former acid.

Phenyl-acetic acid gives a brownish-purple colour. The test will detect 0·5 mgrm., but this amount would not prevent the detection of benzoic acid in a mixture of 0·5 mgrm. of each acid.

Experience has shown that the dilution of a solution containing a known amount of *m*-diamino-benzoic acid is unsatisfactory, and it is better to find the approximate amount of benzoic acid present to within 1 mgrm. by the method of comparison described, and then to take such a quantity of the solution as will contain between 1 and 3 mgrms. Selected standards, containing known amounts of benzoic acid (differing by 0·25 mgrm.), are tested simultaneously with the unknown substance. In this way the quantity of benzoic acid present can be estimated to within 0·125 mgrm.

PART II

THE APPLICATION OF THE TEST TO THE DETECTION AND DETERMINATION OF BENZOIC ACID IN FOODSTUFFS

APPARATUS.—The apparatus used in this laboratory* is shown in the figure. A is a 300 c.c. flask with a stillhead, B, passing through the rubber stopper in the neck of the flask. C is an ordinary calcium chloride tube which is connected with the stillhead as shown. A straight tube, D, passes through a rubber stopper in the outlet of the tube, C. This tube is drawn out a little at its lower end, and has a hole in its side at E. The flask, A, is heated on a wire gauze, and the lower limb of C is immersed in boiling water during the distillation.

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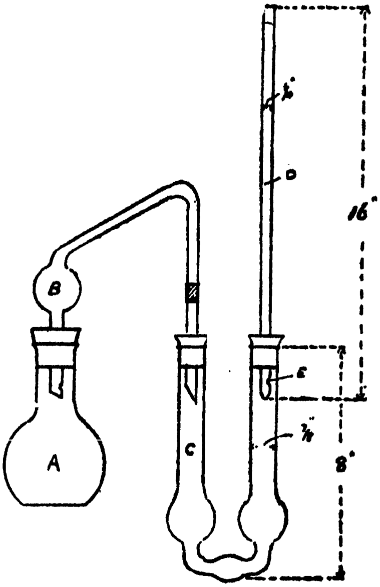
* This apparatus was used some time prior to the publication of Leather's paper (ANALYST, 1931, 56, 299).

The food under examination is placed in A, together with the diluting water, acid, and the required amount of salt to make a saturated solution. A little pumice is also added. A seal is made in the tube, C, by means of $N/1$ sodium hydroxide solution. At the end of the distillation, the contents of the tube, together with the washings of C and D, are either evaporated in a porcelain basin, or made up to a known volume and an aliquot part is taken for evaporation, according to the object of the test. The residue is transferred to a boiling tube by means of water, 2 or 3 c.c. only being required, and Mohler's test is carried out.



Qualitative Application.—Foodstuffs may be tested for absence of benzoic acid by taking 5 grms. in the flask, A, and adding 50 c.c. of water containing 5 c.c. of dilute sulphuric acid, and 20 grms. of salt. One c.c. of N sodium hydroxide solution is introduced into C, with sufficient water to form a seal. (In the case of foodstuffs containing much volatile acid, *e.g.* vinegar, an increased amount of sodium hydroxide must be used. For 5 c.c. of vinegar, 0·5 c.c. of 50 per cent. sodium hydroxide solution is taken.) The duration of the distillation is four minutes. The contents of the tube, C, together with washings, are evaporated and transferred to a boiling tube.

Actual results obtained were as follows:

	Benzoic acid.	
	Added. Mgrm.	Found. Mgrm.
Lime juice	0·5	a little less than 0·5
Coffee extract	0·5	more than 0·25
Butter	0·25	more than 0·2
Brawn (decomposed)	0·5	more than 0·25
Sausages	0·5	a little more than 0·25
Jam	0·5	0·5
Cheese	0·5	a little less than 0·5
Milk (8 minutes' distillation)	0·5 0·25	0·5 0·25
Canned cream	0·25	a little less than 0·25
Cider	0·25	0·25
Bottled fruit	0·5	0·5
Essence of ginger (1 per cent. aqueous solution)	0·5	0·5
Candied peel	0·5	more than 0·25

The above process has to be modified in the following manner when applied to articles of food containing much volatile acid, *e.g.* pickles, sauces, vinegar, etc.:

After the distillation, the contents of tube, C, are transferred to a separator, made acid, and extracted with three portions of 15 c.c. of a mixture of equal parts of ether and petroleum spirit. The combined extracts are washed three times with 1 c.c. of water, and the benzoic acid is then extracted three times with $N/10$ sodium hydroxide solution, 1 c.c. being used for each extraction. The alkaline extracts are collected in a boiling tube and the remainder of the test carried out as described.

	Benzoic acid.	
	Added. Mgrm.	Found. Mgrm.
Vinegar (malt)	0·5	0·5
Sauce (7 minutes' distillation)	0·25	0·25

It is clear from the above results that 50 to 100 parts of benzoic acid per million are easily detected by this process; and should benzoic acid be found, an approximate estimate of the amount present can be obtained.

The presence of salicylic acid (or of any of those substances which give a yellow colour in the test) will not prevent the detection of benzoic acid. The yellow colour becomes orange to deep orange, according to the quantity of benzoic acid present.

Three tests may be quoted:

	Benzoic acid. Mgrms.	Salicylic acid. Mgrms.	Result.
1.	0·5	0·5	Easily detected; colour, orange
2.	2·0	2·0	Easily detected; colour, deep orange
3.	2·0	6·0	Easily detected; colour, orange

These colours cannot be mistaken; once having seen the marked difference between the colour given by benzoic acid and the yellow of salicylic acid, one could never fail to detect the former when present. It is extremely unlikely that excess of salicylic acid would be present.

QUANTITATIVE DETERMINATION.—*General Method.*—The approximate amount of benzoic acid must be known, and, in the majority of cases, the qualitative examination will give this accurately enough for the purpose; but it is suggested that, when dealing with those foods in which benzoic acid is allowed by the Public Health (Preservatives, etc., in Food) Regulations, a combination of the qualitative and quantitative processes be made (*vide infra*).

The approximate amount of benzoic acid having been found, such a quantity of the foodstuff is taken as will contain not more than the amount of benzoic acid given in the following table for the particular article of food under examination. It is better to work with less than the maximum amount.

Maximum amount in mgrms. of benzoic acid that should be distilled.

7 mgrms. for	5 mgrms. for	3 mgrms. for
Lime juice	Marmalade	Vinegar
Cider	Jam	Fats (butter)
Mineral water	Sauce	Margarine, etc.
Non-alcoholic wine	Pickles	Canned cream
Brewed ginger-beer	Brawn	Milk
	Potted meat	Cheese (not more than 2 mgrms.)
	Coffee extract	Cream
	Preserved fruit	All foods containing much volatile fatty acids
		Sausages
		Fish paste

In the case of solids and viscous liquids, *e.g.* coffee extract, 120 c.c. of water, containing 5 c.c. of dilute sulphuric acid (10 per cent.), are used in the flask, A, and enough acid and water to make the total volume 120 c.c. when the food is a liquid. Pumice is added and 40 grms. of salt; 1·5 c.c. of *N* sodium hydroxide solution are placed in the tube, C, with sufficient water to form a seal. The time of the distillation is from 12 to 15 minutes; it is conducted as rapidly as possible, but must be regulated by the behaviour of the condensed liquid in C. The tube, C, should be surrounded by boiling water to such a depth that the bulbs on the vertical limbs are at least half-immersed. The flask, A, and the tube, C, are held by clamps, and the bumping has no ill effects until the boiling is so violent that it forces the liquid in C up through the tube, D. This can be regulated by removing the flame from under the flask, A, for a second or two. It is essential that the distillation be carried on for some minutes after the solution becomes saturated with salt. It will be found convenient to transfer the contents of C, together with the washings of C and D, to a dish, and thence to a graduated flask. A sufficient quantity of this solution to contain 3 mgrms. (or as near as possible to this amount) is taken for comparison with appropriate standards differing from each other by 0·25 mgrm.

There are one or two points with regard to the carrying-out of the Mohler's test which are worthy of notice.

The excess of sodium hydroxide over the benzoic acid should be kept as small as possible. The inside of the boiling tube should be quite dry before the potassium nitrate and sulphuric acid are added. All solutions are added by means of pipettes (or burettes), except the ammonia solution, for which a cylinder is used. The nitration is allowed to proceed for a minute or two, and then the tube is taken out of the water, and the sulphuric acid made to run over its inner surface so as to come in contact with any solid deposited on the upper part of the tube.

The tube should be thoroughly cooled after the addition of the ammonia solution, and before the hydroxylamine hydrochloride is added. After the addition of the latter solution the contents are well mixed.

The temperature of the water-bath in which the reduction is carried out should be at about 80° C. before a dozen tubes are placed therein. The temperature can then be quickly adjusted to 65° C. Six minutes are allowed from the time the tube is placed in the water. At the end of the reduction the tube is cooled before matching. The solution is poured into a 25 c.c. graduated cylinder and adjusted to 15 c.c. by the addition of water (if necessary). It is then transferred to a 50-c.c. Nessler tube. Standards from 2·25 to 3·25 mgrms. are generally needed.

It has been found that attempts to match the standard by dilution are unsatisfactory, presumably owing to the hydrolysis of the amino-compound in such weak solution.

SPECIAL CASES.—1. Vinegar, sauce, etc., which contain an excessive amount of volatile acid, naturally require more sodium hydroxide in the tube, C. About 10 c.c. of *N* sodium hydroxide solution are sufficient except for amounts of vinegar exceeding 10 grms. A little more than the calculated quantity of 50 per cent. sodium hydroxide solution necessary to neutralise the volatile acid content of the amount of vinegar taken is used; 1·5 c.c. of 50 per cent. sodium hydroxide solution have been used for 20 grms.

The contents of C (after the distillation is complete) are transferred to a 100 c.c. stoppered cylinder, acidified and made up to about 100 c.c., salt (30 to 35 grms.) is added, and the whole is well shaken. The solution is extracted 4 or 5 times with 15 to 20 c.c. of a mixture of ether and petroleum spirit (1:1), and these extracts are collected in a separator by blowing off the ethereal layer as in the Werner–Schmid method of extracting fat. The stopper of the cylinder is washed each time before removing it, and also the tube used for blowing over the ethereal extracts. The outlet of the separator should be cut off fairly close to the tap, and a mark made indicating a volume of 1 c.c. The extracts are washed with 3 (in the case of vinegar, 6) separate portions of 1 c.c. of water.* The benzoic acid is re-extracted with 0·5 c.c. of *N* sodium hydroxide solution, and then 5 times with *N*/10 sodium hydroxide solution, 2 c.c. being used for each extraction. For extracts of those substances which have been oxidised it is necessary to use 1·0 c.c. of *N* sodium hydroxide solution for the first extraction.†

After each extraction a little water is allowed to run down the inside of the separator, and drawn off without shaking, thus avoiding loss of any of the alkaline liquid remaining on the outlet of the separator. The ether is finally washed with about 5 c.c. of water, which is then added to the alkaline extracts. It is advisable to test the first extract to make certain that excess of alkali is being used.

2. Fatty acids retard the distillation of benzoic acid, so that butter, canned cream, etc., require a much longer distillation for the same amount of benzoic acid. To this end, a mark is made on the flask, A, indicating the height of its contents before distillation. A brisk distillation is carried out, using 1 c.c. of *N* sodium hydroxide solution in the tube, C, and the apparatus is allowed to cool for a few minutes. The contents of tube, C, with washings, are transferred to a dish. A further 0·5 c.c. of *N* sodium hydroxide solution is added to the tube, which is then again connected with the apparatus. To the flask, A, sufficient water is added to make the contents up to the mark. A second distillation is carried out, and the contents of the tube, C, are added to those from the first distillation. The whole (or part, as the case may be) is evaporated, and the remainder of the process is carried out as usual.

Cheese should be cut up into very small pieces, and the distillations made as described above, but not more than 2 mgrms. of benzoic acid should be distilled.

Two distillations are also necessary when working with sausages and fish paste. Fatty layers seem to retard the distillation of benzoic acid, although no difficulty was experienced when dealing with brawn and potted meat.

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* A similar volume of ether containing 4 mgrms. of benzoic acid was extracted (*a*) with 3 separate portions of 1 c.c. of water; (*b*) a little dilute sulphuric acid was added to the ether, the mixture shaken, and the acid drawn off. Three more aqueous extractions of 1 c.c. each were made; then (*c*) a drop or two of acetic acid was added, and three further extractions were made. These three extracts were tested for benzoic acid by Mohler's test, with the following results:—(*a*) Less than 0·1 mgrm.; about 0·05 mgrm. of benzoic acid. (*b*) Less than 0·03 mgrm. of benzoic acid. (*c*) About 0·03 mgrm. of benzoic acid.

† In two cases additional extractions were made, and no trace of benzoic acid was detected, thus indicating that the extraction had been quantitative.

3. In the presence of salicylic acid, the distillate is transferred to a small beaker, and strong potassium permanganate solution is added until a permanent pink is obtained. The temperature should be between 40 and 50° C. The excess of permanganate is destroyed with sodium sulphite (as small a quantity as possible) after transferring to a stoppered cylinder, and the liquid is acidified with dilute sulphuric acid, saturated with salt, and extracted with the mixture of ether and petroleum spirit. (Dr. Monier-Williams' Report, 39.) The ethereal extracts are treated as described under vinegar.

Blank determinations have been made upon articles of food free from benzoic acid, 20 grms. being taken in all cases. Cider, canned cream, brawn, sauce, malt vinegar, sausages, and butter gave no more than a slight coloration, when treated by the method above described for the particular food under examination.

Coffee extract,* lime juice and marmalade gave a yellow colour. In the case of routine examination, with the object of finding out whether a sample contains less than the limit of benzoic acid allowed by the Regulations, the above colours may be neglected. In general, the results will be high.

An alkaline oxidation is necessary when the amount of benzoic acid has to be determined with greater accuracy.

An oxidation is also necessary in the case of cider, jam, fish paste, preserved fruit, non-alcoholic wine, mineral water, and brewed ginger-beer.

The nitrated solution, before the addition of the 2 c.c. of water, should be free from colour, or, at the most, should only be very faintly coloured.

It will be noted that a butter, to which was added 50 mgrms. of soluble volatile fatty acids from a Reichert distillation, gave a distillate in which the full amount of benzoic acid present was detected. The distillation was continued for 10 minutes.

The amount of 3 mgrms. has been used as a working quantity in these determinations, because the depth of colour given by 4 to 5 mgrms. renders the detection of parts of a mgrm. impossible, and, as stated previously, dilution is unsatisfactory.

The following method should prove sufficiently accurate for sorting out those samples which fulfil the requirements of the Regulations from those which fail to do so:—Five grms. of food are taken, and the same amount of acid, water and salt as for the qualitative estimation, and the same time taken for distillation. The whole of the distillate is used for the Mohler's test, and the quantity of benzoic acid (if present) is determined by means of the ferric thiocyanate solution. It should be mentioned that the colour of the ferric standards in very dilute solution is not the same as that due to *m*-diamino-benzoic acid, but, even so, there is no difficulty in estimating the amount of benzoic acid present in these small amounts.

When dealing with rancid fats it is essential that the distillations should be short, but as brisk as possible, and less than 2 mgrms. of benzoic acid should be distilled.

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* Care should be taken in the distillation of coffee extract, as excessive frothing takes place on the point of boiling. The flame should be removed for a second or two when boiling commences.

RESULTS OBTAINED BY THE APPLICATION OF THE ABOVE METHODS

	Article of food and weight taken.	Benzoic acid				
		Mgrms. in aliquot part taken		Parts per million		Percentage error
		Added	Found	Added	Found	
*1.	Lime juice (10 grms.)	3·18	3·5	500	550	+10·0
*2.	,, ,, (15 grms.)	3·27	3·37	300	308	+ 2·7
*3.	Cider (10 grms.)	2·91	3·25	400	446	+11·5
*4.	Marmalade (20 grms.)	2·5	2·62	250	262	+ 4·8
5.	Sauce (15 grms.)	2·8	2·63	267	250	− 6·3
6.	Butter (10 grms.), containing 50 mgrms. of soluble volatile fatty acids	0·5	0·5	—	—	—
7.	Lime juice (20 grms.), containing 10 mgrms. of salicylic acid ..	1·9	2·0	190	200	+ 5·2
8.	Butter (15 grms.)	3·0	2·75	200	183	− 8·5
*9.	Marmalade (10 grms.)	3·0	3·12	300	312	+ 4·0
10.	Canned cream (15 grms.) ..	3·5	3·25	233	217	− 6·8
11.	Malt vinegar (10 grms.)	3·0	3·25	300	325	+ 8·3
12.	Lime juice (10 grms.)	3·06	3·25	510	541	+ 6·0
13.	Cider (10 grms.)	3·05	2·8	610	560	− 8·2
14.	Mixed pickles (20 grms.) ..	2·8	2·87	200	205	+ 2·5
15.	Coffee extract (15 grms.) ..	2·94	2·7	280	257	− 8·2
*16.	Jam (30 grms.)	1·5	1·7	50	57	+14·0
17.	Marmalade (20 grms.)	2·8	2·87	200	205	+ 2·5
*18.	Milk (10 grms.)	2·7	2·87	270	287	+ 6·3
19.	Sausage (15 grms.)	2·7	2·75	180	183	+ 1·7
20.	Butter (10 grms.)	2·7	2·85	270	285	+ 5·5
21.	Malt vinegar (15 grms.)	2·5	2·62	167	175	+ 4·8
22.	Cheese (10 grms.)	1·5	1·38	150	138	− 8·0
23.	Fish paste (10 grms.)	2·5	2·37	250	237	− 5·2
24.	Cider (10 grms.)	4·0	4·3	400	430	+ 7·5
*25.	Potted meat (10 grms.)	2·7	3·0	450	500	+11·0
26.	Sauce (30 grms.)	1·5	1·12	50	37	−26·0
27.	Preserved fruit (15 grms.) ..	2·25	2·37	300	316	+ 5·3
28.	Butter (10 grms.)	2·25	2·0	225	200	−11·1
29.	Pickles (20 grms.)	2·45	2·25	175	160	− 8·8
30.	Butter (10 grms.)	2·5	2·0	250	200	−20·0
31.	Butter (10 grms.)	1·5	1·25	150	125	−16·6

* The determinations marked with an asterisk were carried out by the general method.

Nos. 7, 12, 13, 15, 17, 24, 27 .. .. oxidation after distillation.
Nos. 5, 11, 14, 23, 26, 29 .. .. extraction with petroleum spirit and ether after distillation.
Nos. 8, 10, 19, 20, 22, 23, 28, 30, 31 .. two distillations carried out.

There are indications that it is better to work with the least possible excess of acid in the distillation flask when dealing with butter and rancid fats. In experiment No. 30, 2 c.c. of *N* sulphuric acid were used instead of 5 c.c. of dilute acid; and in No. 31, which was a very rancid butter, only 1 c.c. of *N* sulphuric acid was used.

My thanks are due to Mr. D. R. Wood, F.I.C., for his very helpful criticisms, and I have to acknowledge the assistance of Mr. A. E. Fletcher, F.I.C., in carrying out some of the experimental work.

THE SOMERSET COUNTY LABORATORIES,
WESTON-SUPER-MARE.

The Composition of Linseed Oil

BY N. E. COCCHINARAS, PH.D.

(*Read at the Meeting, December* 2, 1931)

THE composition of linseed oil has been the subject of many investigations, and, as shown in the tabulated results given below, very conflicting conclusions have been arrived at.

For the purposes of a research, shortly to be published elsewhere, on the hydrogenation of linseed oil, it became necessary to have as accurate a knowledge as possible of the composition of linseed oil, and to examine critically the methods available for its analysis.

The following is a short account of the work carried out for this purpose.

The linseed oil used was from Argentine (La Plata) linseed, and was supplied by the British Oil and Cake Mills Co., Ltd.

It had (i) refractive index 1·4729 at 40° C.; (ii) flash point 230° C.; (iii) specific gravity 0·9320 at 15·5° C.; and (iv) saponification value 192. The acid value was negligible.

PART I

(1) FATTY ACIDS PRESENT IN LINSEED OIL

The following table contains published analyses of linseed oils and the analytical figures of the linseed oil used in this research:

(*For Table see next page.*)

(2) ATTEMPTED ISOLATION OF LINOLENIC ACID FROM THE UNSATURATED FATTY ACIDS OF LINSEED OIL

(*a*) ISOMERIDES OF THE LINOLENIC ACID OF LINSEED OIL.—In recent years the isomerism of linolenic acid has been extensively investigated. When an ethereal solution of the unsaturated fatty acids of linseed oil is brominated, a crystalline hexabromide (m.pt., 183° C.) separates. When this hexabromide is debrominated an acid (b.pt., 230–232° C. at 17 mm.) is obtained. This, on rebromination, might be expected to yield the theoretical amount of solid hexabromide, but it gives only 23 per cent. of crystalline hexabromide (m.pt., 183° C.) and 77 per cent. of a liquid hexabromide.

The question is: Do the unsaturated fatty acids of linseed oil contain 2 linolenic acids (isomers), one of which, on bromination, gives a crystalline hexabromide, and the other a liquid hexabromide; or do they contain one linolenic acid which, on bromination, gives the theoretical amount of hexabromide, which hexabromide, when debrominated, gives rise to two isomeric linolenic acids, one of which gives a crystalline, and the other a liquid hexabromide? The question is of importance, because on the answer to it depends the determination of linolenic acid in linseed oil.

	Iodine value of oil.	Saturated acids and unsaponifiable matter.	Glyceryl radicle.	Oleic acid.	α-Linolic acid.	β-Linolic acid.	α-Linolenic acid.	β-Linolenic acid.	Palmitic acid.	Stearic acid.	Myristic acid.	Arachidic acid.	Ether-insoluble bromides in oil.	Ether-insoluble bromides of mixed acids.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Friend (*Chemistry of Linseed Oil*)	180	10	4·6	5·0	48·3		32·1		—	—	—	—	—	—
Coffey,[3] oxygen method	—	8·1	4·3	5·0	48·5		34·1		—	—	—	—	—	—
Mulder[4]	—	—	—	—	—	—	—	—	5	—	5	—	—	—
Haller[4]	—	—	—	—	—	—	—	—	—	—	—	small amount	—	—
Fahrion[6]	—	9·9	4·6	17·5	30		38		—	—	—	—	—	—
Lewkowitsch[6]	190·4	8·9 7·5	—	—	—	—	15·4	14	—	—	—	—	41·9	38·1
Morrell[7]	—	—	—	4	—	—	—	—	20	51·7	—	—	—	—
Eibner and					58·8		22·8							
Schmidinger	—	8·3	4·1	4·5	17	41·8	20·1	2·7	—	—	—	—	—	—
Hazura[8]	—	10	—	5	15		15	55	—	—	—	—	—	—
R. F. Morrell[6]	—	—	—	—	—	—	—	—	—	—	—	could not be detected	—	—
Hehner[9] and Mitchell	—	—	—	—	—	—	—	—	—	—	—	—	23·8 25·8	—
Ingle[10]	—	—	—	—	—	—	—	—	—	—	—	—	33·7 48·1	—
Sutcliffe[11]	—	—	—	—	—	—	—	—	—	—	—	—	41·6 49·3	—
Present research	179·9	9·7	—	2·3	69·6		18·47		6·7	3·0	—	—	—	

Hazura[2] oxidised the unsaturated fatty acids of linseed oil, and obtained two hexahydroxy-stearic acids, linusic acid (m.pt., 203° C.) and isolinusic acid (m.pt., 173° C.), and, therefore, concluded that there are two isomeric linolenic acids in the unsaturated acids of linseed oil. From the quantities of oxidation and bromination products obtained, Hazura estimated the composition of the oil to be as follows: Oleic acid, 5; linolic acid, 15; α-linolenic acid, 15; β-linolenic acid, 55; and saturated acids, 10 per cent.; but this composition would require a much higher iodine value than is found experimentally.

Erdmann and Bedford[3] assume the existence of two linolenic acids, which they differentiate as α- and β-linolenic acids. They conclude that the α-acid occurs in linseed oil, and that, when brominated, it yields a quantitative amount of the crystalline hexabromide (m.pt., 183° C.). Since the linolenic acid from this hexabromide yields, on re-bromination, only 23 per cent. of the theoretical hexabromide, they assume that the remaining 77 per cent. consists of a liquid β-linolenic acid hexabromide. These isomeric relations were the subject of a controversy between Erdmann and Rollett.[4]

Rollett assumes that, on bromination, the linolenic acid in the unsaturated fatty acids of linseed oil yields four isomeric hexabromides. If only one of the assumed isomerides is crystalline, a yield of 23 per cent. of hexabromide, as found by experiment, would be obtained. According to Erdmann, this assumption appears to be unwarranted, since the *α*-linolenic acid obtained by the fractional crystallisation of the zinc salts of the unsaturated fatty acids of linseed oil gives, on bromination, the theoretical quantity of hexabromide.

The amount of the zinc salt $(C_{18}H_{29}O_2)_2Zn,\frac{1}{2}ZnO$, (m.pt., 72–73° C.) isolated corresponded with the presence of 18 per cent. of linolenic acid in the unsaturated fatty acids.

S. Coffey,[5] however, was unable to confirm this statement of Erdmann.

Erdmann and Bedford asserted that the 77 per cent. of the liquid bromide resulting on brominating the linolenic acid obtained from the crystalline hexabromide, was not a hexabromide, but a tetrabromide.

Rollett proved that this oily bromide is not a tetrabromide, but an unsaturated substance which absorbs more bromine, finally yielding a hexabromo derivative.

The following experiments were carried out to ascertain whether this substance is a hexabromide, and not a liquid tetrabromide, or an unsaturated substance which still absorbs bromine:

Five grms. of the pure hexabromide (m.pt., 183° C.), obtained by brominating the fatty acids of linseed oil, 120 c.c. of 96 per cent. alcohol, and 20 grms. of granulated zinc were kept boiling under a reflux condenser for 24 hours until a clear solution was obtained. The solution was poured into water, the oily layer (consisting of a mixture of the ethyl ester and the zinc salt of linolenic acid) was shaken with warm dilute sulphuric acid, and the oil which separated was saponified with alcoholic potash. The potassium salt was decomposed, and the linolenic acid taken up with ether and dried, the ether evaporated in the presence of hydrogen, and the linolenic acid distilled in a high vacuum. The acid had iodine value 266 (theor. 273·9).

To 0·194 grm. of this acid, dissolved in 20 c.c. of ether and cooled to $-5°$ C., bromine was added, drop by drop, until a brown coloration persisted. The solution was allowed to stand for 22 hours. The deposited crystalline precipitate was filtered off, washed and dried.

From 0·194 grm. of the acid, 0·069 grm. of crystalline hexabromide (m.pt., 183° C.) was obtained. The filtrate, on concentration, yielded a further 0·0602 grm. of the substance melting at 183° C.

Total weight of the precipitate = 0·1292 grm. = 25 per cent. yield.

After evaporation of the solvent and excess of bromine from the filtrate, the oily residue was found to contain 60·47 per cent. of bromine (Carius). (Theor. for linolenic acid hexabromide, 63·32 per cent.)

This residue contains 6 atoms of bromine, and not 4, as originally stated by Erdmann and Bedford.

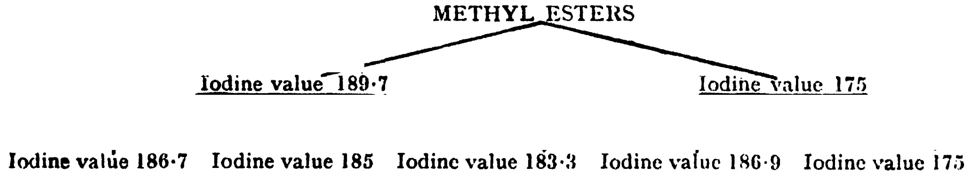
(*b*) THE FRACTIONAL DISTILLATION OF THE METHYL ESTERS OF THE UNSATURATED FATTY ACIDS.—A modern method of examination of fatty acids is by fractional distillation of the methyl esters. This method has been applied with success to the examination of coconut and palm-kernel oils, which are composed of lower fatty acids and myristic, palmitic and oleic acids, the boiling points of the methyl esters of which differ considerably.

The boiling points of the methyl esters of the unsaturated acids of linseed oil lie so closely together that an attempted separation, which is described in the following experiment, did not meet with success:

Twenty grms. of the unsaturated acids were dissolved in 45 c.c. of methyl alcohol, containing 5 per cent. of concentrated sulphuric acid, and heated for two hours under a reflux condenser. The excess of alcohol was removed by distillation, the residue dissolved in ether, the ethereal solution washed and dried, and the ether evaporated.

The flask containing the crude methyl esters was connected with a distillation triangle and exhausted by means of an oil pump. The distillation was carried out slowly at a pressure of 0·1 to 0·3 mm.

The following diagram gives iodine values of the various fractions obtained:



The theoretical iodine values of the methyl esters are:

Methyl oleate	Iodine value	85·8
Methyl linolate	„ „	172·8
Methyl linolenate ..	„ „	260

The results of the distillation show that it is difficult to separate methyl linolenate from the methyl esters of the other unsaturated acids, because the boiling points of the esters lie so close together.

(*c*) PREPARATION OF SOME METALLIC SALTS OF THE UNSATURATED FATTY ACIDS.—The following metallic salts of the acids were prepared with the object of effecting a separation by fractional crystallisation in various solvents. The unsaturated acids were obtained from the linseed oil by Tortelli's lead salt and ether method:

Cadmium Salts.—Five grms. of unsaturated acids were dissolved in aqueous ammonia, and the ammonium salts were poured into an aqueous solution of cadmium sulphate containing 5·3 grms. of $CdSO_44H_2O$.

The precipitated cadmium salts were filtered off, washed and dried (m.pt., 200° C.). They were insoluble in the following organic solvents: Methyl and ethyl alcohol, acetone, ethyl acetate, benzine, carbon tetrachloride, petroleum spirit, amyl alcohol, and mixtures of these solvents.

Mercury Salts.—The ammonium salts of 5 grms. of unsaturated acids were poured into an aqueous solution containing 5 grms. of mercurous chloride. Amorphous mercury salts were precipitated. No attempts were made to crystallise them.

Beryllium Salts.—Twelve grms. of the acids were converted into ammonium salts, and the excess of ammonia driven off on the water-bath. The salts were gradually poured into a solution of 10 grms. of beryllium nitrate, and the precipitated beryllium salts were filtered off, washed and dried (m.pt., 105° C.). The object of preparing the beryllium salts was to see whether they could be distilled under reduced pressure, and, if so, whether a separation could be effected. The beryllium salts, however, decomposed on heating under reduced pressure.

Magnesium Salts.—Six grms. of ammonium salts of the unsaturated acids were poured into an aqueous solution of 8 grms. of magnesium sulphate. The precipitated magnesium salts were filtered off, washed and dried. It was not possible to dissolve them completely in any of the several organic solvents used.

PART II

THE SEPARATION OF THE UNSATURATED AND SATURATED FATTY ACIDS OF LINSEED OIL

The separation of the unsaturated from the saturated acids was carried out by the "lead salt and ether" method as follows:

The linseed oil (21·5 grms.) was saponified with alcoholic potash, the soap solution was slightly acidified with acetic acid, and, finally, titrated to neutrality with alcoholic potash. The alcohol was distilled in the presence of hydrogen, and the soap solution was diluted with water, and treated with a slight excess of a 10 per cent. boiling aqueous solution of lead acetate.

The flask was allowed to cool, and the lead soaps filtered off, washed with hot water, and warmed on the water-bath with 200 c.c. of ether, allowed to stand overnight in the presence of hydrogen, and the solution was then filtered and treated with dilute acid, and the liberated fatty acids were washed, dried in presence of hydrogen and weighed, (A).

The ether-insoluble lead salts were warmed on the water-bath for some time with 100 c.c. of ether, allowed to cool, and the liquid filtered, (B).

The filtrate was concentrated and decomposed with dilute acid, and the liberated fatty acids were united with fraction (A), and their iodine value determined.

	Per Cent.	Iodine value.
Proportion of unsaturated acids	90·3	190
„ „ saturated acids (by differ.) ..	9·7	

The iodine value of the saturated acids was practically negligible.

PART III

THE OXIDATION AND DETERMINATION OF THE PERCENTAGE COMPOSITION OF THE UNSATURATED FATTY ACIDS OF LINSEED OIL

The unsaturated fatty acids present in the linseed oil under examination were identified by the m.pt. of their oxidation products obtained by the method described by Lewkowitsch.

The following is the method which was adopted for the determination of the percentage composition of the mixture of linolenic, linolic and oleic acids:

The unsaturated acids (0·1552 grm.) were dissolved in 20 c.c. of ether containing 1 c.c. of glacial acetic acid, and cooled to –5° C., and bromine was added, drop by drop, until a red coloration persisted. The flask was then allowed to stand for 4 hours at about 0° C., the solution was filtered, and the precipitate washed with chilled ether till free from excess of bromine, dried in the oven and weighed. From 0·1552 grm. of the acids 0·063 grm. of crystalline hexabromide (m.pt., 183° C.) was obtained, which corresponds to 40·6 per cent. ≡ 14·89 per cent. linolenic acid.

In view of the difference in opinion whether glacial acetic acid increases or decreases the yield of hexabromide, the following experiment was carried out, the same method as above, but without glacial acetic acid, being used:

From 1·109 grm. of the acids 0·5584 grm. of crystalline hexabromide, corresponding to 18·47 per cent. of linolenic acid (bromine in hexabromide, 63·32 per cent.).

Therefore, the yield of solid hexabromide, when ether without acetic acid is used, is higher than the yield obtained in presence of acetic acid.

Examination of the Filtrate.—The solvent and excess of bromine were driven off under reduced pressure. The residue was an oily mixture of bromides. The bromine content of this mixture of bromides, as determined by the Carius method, was 52·8 per cent.

From the percentage of bromine in the mixture of bromides the percentages of oleic and linolic acids can be calculated, assuming the absence of any hexabromide, by means of the following equation:

$$x + y = 100$$
$$0{\cdot}3618x + 0{\cdot}5333y = 52{\cdot}8,$$

where x represents oleic acid and y linolic acid. Whence $x = 3{\cdot}1$ per cent. and $y = 96{\cdot}9$ per cent.

The composition of the mixed unsaturated acids, calculated from the above equation, is as follows:

Linolenic acid,	18·47 per cent.	(calculated from the yield of crystalline hexabromide).
Oleic acid,	2·53 ,, ,,	(calculated from the residual oily bromides).
Linolic acid,	79·0 per cent.	

The bromine content excludes the presence of liquid hexabromide, unless the amount of oleic acid present in linseed oil exceeds 5 per cent.

Apart from amount calculated by Fahrion, the highest content recorded of oleic acid present in linseed oil is 5 per cent., as shown in the figures on p. 234.

The amount of dihydroxy-stearic acid (m.pt., 137° C.) which was found by the oxidation of the mixed unsaturated acids with alkaline permanganate was very small indeed. The method, however, is not recommended for quantitative experiments.

It was, therefore, thought necessary to determine the approximate percentage of oleic acid by an indirect method.

The only available method of isolating oleic acid is that of Farnsteiner, which is based on the insolubility of barium oleate and the barium salts of saturated acids in benzene containing 5 per cent. of alcohol.

The following experiment was made in order to determine approximately the quantity of oleic acid present in linseed oil:

One hundred grms. of linseed oil were saponified with the equivalent amount of baryta in a mixture of petroleum spirit and alcohol (1:1) by heating under a reflux condenser on the water-bath for 4 hours, until saponification was complete. The soap solution was allowed to stand overnight. The precipitated salts were filtered off, decomposed with hydrochloric acid, washed and dried. The amount of acids obtained was 14·8 grms.

Presumably, the acids so obtained were saturated acids and oleic acids. They were converted into their lead salts by adding the equivalent amount of lead acetate to a solution of ammonium salts of the acids. The dry lead salts were warmed on the water-bath with 200 c.c. of ether and allowed to stand overnight.

The ether-soluble lead salts were decomposed with dilute acid; the acids so obtained had an iodine value of 143, and weighed 6·5 grms.

The acids were warmed on the water-bath up to 30° C. with a solution of sodium nitrite in 30 per cent. nitric acid in order to convert the oleic acid present into elaidic acid. On cooling, the oily layer became semi-solid. It was dissolved in absolute alcohol, and, on freezing, 1·5 grm. of elaidic acid was precipitated. The precipitate (m.pt., 45° C.) corresponded with a yield of 1·5 per cent.

The ether-insoluble lead salts, on being decomposed, gave 8 grms. of saturated acids, which had an iodine value of 29.

From the filtrate containing the barium salts soluble in benzene and alcohol, 120 grms. of salts were precipitated; these were decomposed, and 74 grms. of unsaturated acids were obtained, which, on treatment with sodium nitrite in nitric acid, gave only a negligible further quantity of elaidic acid.

The above experiment, therefore, has proved that oleic acid occurs only in very small proportions amongst the fatty acids of linseed oil.

Rollett's theory, referred to on p. 235, cannot hold, because if, on brominating linolenic acid, four bromine derivatives were produced, the bromine content of the oily residue, after filtering the crystalline bromide, would be much higher.

Also, assuming there was a β-linolenic acid present in the mixed fatty acids which would absorb six atoms of bromine, the residual bromides, after filtering off the crystalline bromide, would have a much higher bromine content than that actually found (52·8 per cent.).

The above evidence may be taken as conclusive that the linolenic acid present in the fatty acids of linseed oil, on bromination, yields quantitatively the crystalline hexabromide, m.pt., 183° C.

PART IV

THE DETERMINATION OF THE RELATIVE PROPORTIONS OF THE DIFFERENT SATURATED FATTY ACIDS

Mulder[6] claimed to have isolated palmitic and myristic acids in equal proportions by fractional crystallisation from alcohol of the saturated acids, separated from the unsaturated acids by the "lead salt and ether" method. He found no stearic acid.

The occurrence of stearic acid was proved by Haller, who separated by fractional distillation the methyl esters of the saturated acids of linseed oil, and obtained methyl palmitate, methyl stearate and methyl arachidate.

Haller[6] concluded that stearic acid was present in appreciable quantities, but, of arachidic acid, only traces were found. Morrell[7] isolated stearic and palmitic acids, but could not detect myristic or arachidic acid.

Various methods have been proposed from time to time for the separation of the mixed saturated acids, but none of them proved successful. If it is only a case of identification, the saturated acids can be separated by fractional precipitation from their alcoholic solutions with hot alcoholic solutions of barium or magnesium acetate.

Berg and Fahrion[6] suggest the separation of palmitic from stearic acid by the difference of their solubility in acetone.

Twitchell published a method for the identification of individual acids in mixtures, by the depression of their melting points caused by the addition of a known amount of a pure acid.

Holland[6] did not report favourably on the fractional distillation of the mixed solid acids, with a view to isolating the individual acids. His chief objection to the method was the difficulty of obtaining suitable distillation apparatus, and, therefore, the danger of having a plugged apparatus at a high temperature. He attempted to heat the fractionating column and keep the acids liquid by means of a hot-water jacket, as also by an electrically-heated asbestos covering, but neither fully met his requirements.

The examination of the saturated acids of linseed oil was carried out as follows:—Four hundred grms. of linseed oil were saponified with alcoholic potash. The salts were decomposed with dilute acid, the fatty acids were taken up with ether, the ethereal solution was washed with water, and the ether was distilled in presence of hydrogen. There were thus obtained 388 grms. of acids.

A warm alcoholic solution, containing a slight excess of lead acetate over the theoretical quantity, was added to an alcoholic solution of the fatty acids (proportion, 12 alcohol : 1 acid).

The precipitated lead salts were allowed to stand overnight, filtered and recrystallised from alcohol (proportion, 10 alcohol : 1 acid). On cooling, the precipitated lead salts were re-crystallised from alcohol (6 alcohol : 1 acid), and decomposed with dilute acid.

The saturated acids thus obtained (33·5 grms.) melted at 56 to 57° C., and had iodine value, 1·7 (FRACTION I).

The fraction containing the soluble lead salts of the acids was decomposed and the acids recovered (FRACTION II).

The lead salt of arachidic acid is insoluble, and the lead salts of palmitic and stearic acids are almost insoluble in 96 per cent. alcohol, whereas lead myristate is soluble in alcohol of that strength. If, therefore, arachidic acid is present in linseed oil it would obviously be among the acids of Fraction I, whilst myristic acid, if present, would be among the acids of Fraction II.

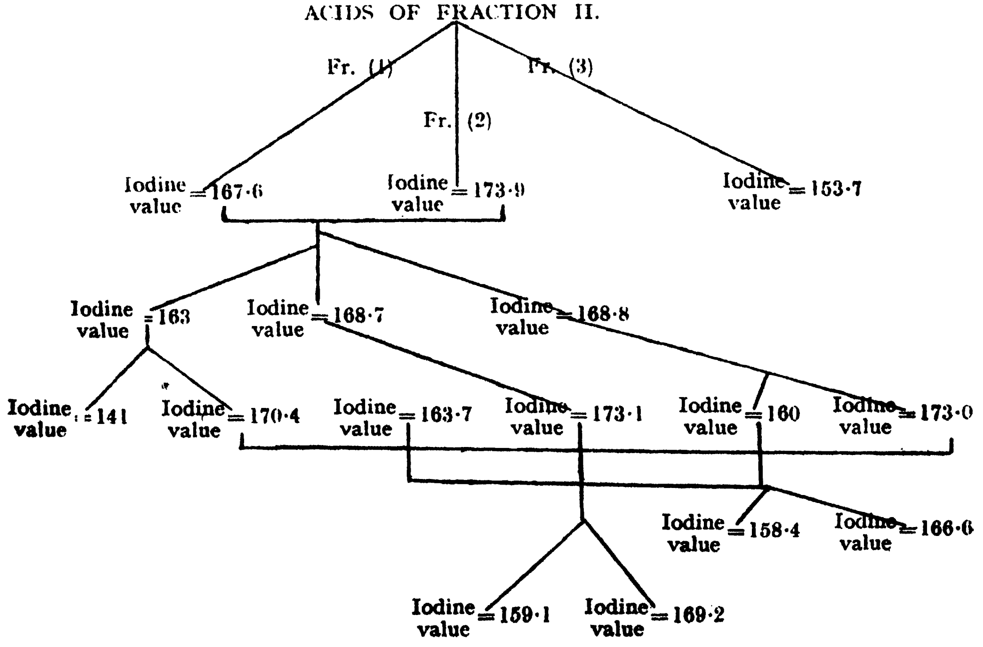
The following table gives the boiling points of the fatty acids concerned:

	Boiling points.			
	Below. 0·2 mm. °C.	2 mm. °C.	14 mm. °C.	15 mm. °C.
Arachidic ..				243
Stearic	154–5			232
Palmitic ..	138–9			215
Myristic	121–2			196·5
(9, 10) Oleic ..	153	163–165		232·5
Linolic			228	
Linolenic ..		205		

From the difference between the boiling points of the unsaturated acids and of myristic acid, it is evident that it should be possible to isolate myristic acid.

The flask containing the acids of Fraction II was attached to a fractionating column (55 inches long), the exterior of which was covered with asbestos fibre to restrict loss of heat by radiation. The acids were very slowly distilled at a reduced pressure (15 mm.) in an atmosphere of hydrogen.

The following is a diagram of the distillation fractions and iodine values of each fraction:



Fraction (3) gave a small amount of a crystalline deposit (m.pt., 66° C.). Nothing more could be separated from the filtrate. Myristic acid could not be detected.

EXAMINATION OF THE ACIDS OF FRACTION I.—The method adopted for the quantitative separation of the saturated acids was the distillation of the acids themselves of the Fraction I under reduced pressure, using a specially devised fractionating column.

The fractionating column consisted of an ordinary column surrounded by an air-jacket, which was exhausted by means of an oil pump and maintained at a good vacuum during the distillation.

In order to prevent bumping, a current of hydrogen was passed through the acids during distillation. The apparatus was attached to a water pump, and a pressure of about 16 mm. was maintained throughout the distillation. The first drops came over at about 220° C. The distillation proceeded slowly, the temperature remaining almost constant (to within 2–3° C.). When the temperature rose nearly to the boiling point of stearic acid (232° C.) the receiver was changed, and the distillation was continued to the end.

The quantitative and qualitative results of the distillation were as follows:

	Grms.
Mixed saturated acids distilled	25·0
Residue in distillation flask	2·8
∴ mixed fatty acids distilled ..	22·2

1st Fraction, 15·23 grms.; melting at 59°–60° C. ("K" palmitic acid, m.pt. 61·9° C.); equivalent weight, 267 (palmitic acid = 256·26).

2nd Fraction, 7·0 grms.; melting at 65° C. ("K" stearic acid, m.pt., 69·3° C.); equivalent weight, 281·74 (stearic acid, 284·29).

The melting points of the acids were sharp. The somewhat high equivalent weight of palmitic acid may be due to the presence of minute traces of unsaturated acids.

The results of the examination of the saturated acids of linseed oil show the presence of stearic and palmitic acids, whilst they confirm the conclusion that myristic and arachidic acids are not present in appreciable amounts. From the results of the distillation the composition of the mixed saturated acids is as follows: —Palmitic acid, 68·5; stearic acid, 31·5 per cent.

With regard to the absence of any isolinolenic acid from the unsaturated fatty acids of linseed oil, referred to on p. 239, and deduced from the bromine content of the mixed liquid bromides, the conclusion reached depends on the validity of the assumption that isomers of linolenic acid would, on bromination, absorb six atoms of bromine.

This assumption is based on the experimental evidence described on p. 235.

Whilst absolute accuracy cannot be claimed for the composition suggested, the iodine value of the oil calculated therefrom differing slightly from that determined experimentally, the results are based on much more comprehensive

analytical data, and are, therefore, probably much nearer the truth than those hitherto published.

The author wishes to express his thanks to Dr. H. Phillips and to Mr. W. H. Simmons for their interest in this work.

BATTERSEA POLYTECHNIC.

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DISCUSSION

Dr. C. A. MITCHELL congratulated the author upon the way in which he had used a variety of weapons in his attack upon one particular problem, and considered that, as regards the amount of oleic acid in linseed oil, he had proved his contention. In his (the speaker's) opinion, however, he had left the other problem still unsettled. The percentage of bromine found in the rebrominated acid was too low, and it was possible that this might be an indication of isomerisation, and that the isomer formed behaved towards bromine solution in a manner analogous to elaeostearic acid, rapidly attaching bromine to 4 of its unsaturated bonds, and then very gradually completing the absorption. It had been found by Toms (ANALYST, 1928, **53**, 75) that bromine in the form of vapour was more rapidly and completely absorbed by tung oil and elaeostearic acid than was bromine in solution. This was found by Croxford (ANALYST, 1929, **54**, 448) to apply also to other oils in which the unsaturated bond occurred next to the carboxyl group, as, for example, croton oil and its fatty acid, tiglic acid. It was possible that parallel tests with bromine vapour and bromine solution would also determine the question whether Rollett was right in concluding that tetrabromides were present, or whether these were only intermediate products. Also, similar parallel tests applied to the mixed fatty acids of the original linseed oil might confirm the author's conclusion that there was no β-linolenic acid originally present. The iodine value of the fatty acids, calculated from the author's percentage results, was lower than one would anticipate for acids from an oil with an iodine value of 180.

Mr. W. H. SIMMONS agreed that the question of the isomer of linolenic acid had not been definitely settled, although he thought that probably Dr. Cocchinaras was right. A good deal of this work, which had occupied a long time, had given negative results, but he thought that it showed the direction which should be taken in investigating the problem.

Mr. E. R. BOLTON agreed with Dr. Mitchell that the use of a bromine method, such as that of Toms, as supplementary to the author's work, would be likely to afford useful information. The re-bromination of the fatty acids from fish oils and other oils yielding octobromides might also prove valuable as a means of determining the relative proportions of oils in mixtures of linseed oil with oils containing highly unsaturated compounds.

Miss LEWKOWITSCH thought that the author was to be congratulated on the definite information he had obtained by the application of Farnsteiner's method of determining oleic acid. De-bromination and re-bromination of the residue left after separation of the hexabromide would have afforded a check on the results.

Mr. K. A. Williams said that he was particularly interested in the fact that the author had demonstrated that only one of the two isomeric forms of linolenic acid was present in linseed oil, and he expected that future research would show that this applied also to other oils containing this acid. He compared the case of oleic acid (which also occurred in one form in nature) with this, and suggested that it would probably be found that the natural forms of linolenic acid and oleic acid were of similar steric configuration.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE BEHAVIOUR OF PHENOLPHTHALEIN AND METHYL ORANGE IN THE OXIDATION OF SUGARS BY ALKALINE IODINE

In the course of an investigation of the iodimetric method for the determination of sugars I have found a divergence of practice in the indicator used when neutralising free acid present as the result of preliminary treatment of the solution (*e.g.* for hydrolysis of sucrose). Kolthoff (*Z. Untersuch. Nahr. Genussm.*, 1923, **45**, 141; Analyst, 1923, **48**, 386) used methyl orange, whilst Richmond and Ellison (Analyst, 1925, **50**, 17) and Slater and Acree (*Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 274; see also Kline and Acree, *ibid.*, **3**, 413) used phenolphthalein. These indicators, in the subsequent oxidation, become a potential source of error if they iodinate readily. Classen and Löb (*Ber.*, 1895, **28**, 1609) have shown that iodination takes place easily with phenolphthalein. Experiments have proved that, under the conditions of the oxidation reaction, tetraiodophenolphthalein is readily formed, whereas the methyl orange is only very slightly acted upon. This may be demonstrated by adding a drop or two of indicator to the alkaline iodine solution and allowing the mixture to stand as in a sugar oxidation. After acidifying with dilute sulphuric acid, and removing iodine with sodium thiosulphate, the liquid is again made alkaline with sodium hydroxide. When phenolphthalein is used a pale lavender blue colour (due to tetraiodophenolphthalein) appears, in place of the pink of phenolphthalein itself. Methyl orange, under similar conditions, gives a pink colour in the acid solution and a yellow in the alkaline, showing the presence of unchanged methyl orange.

A further source of error with phenolphthalein is the introduction of alcohol into the alkaline iodine. This danger is referred to by Kline and Acree (*loc. cit.*), who, for this reason, advise the use of only one drop of indicator. I have proved that even one drop can introduce an appreciable error. With two or three drops the smell of iodoform is detectable, in addition to the presence of tetraiodophenolphthalein.

The following table shows the results of experiments made with 50 per cent. methylated spirit, 0·05 per cent. solution of phenolphthalein in 50 per cent. spirit and 0·05 per cent. solution of methyl orange in water. The experiments were carried out as follows:—Twenty-five c.c. of water with 25 c.c. of standard iodine (approximately 0·08 *N*) and 25 c.c. of sodium hydroxide solution (approximately 0·1 *N*) were allowed to stand for 20 minutes in the presence of varying quantities of the alcohol or indicator. The solution was then acidified and the liberated iodine titrated with standard sodium thiosulphate (approximately 0·05 *N*).

Thiosulphate (0·05 *N*) *equivalent to iodine remaining from* 25 *c.c.* (0·08 *N*) *after* 20 *minutes*

Drops added	50 per cent. spirit c.c.	Phenol-phthalein c.c.	Methyl orange c.c.
0	39·99	39·97	39·99
1	40·02	39·90	39·99
2	39·87	39·81	40·01
3	39·89	39·66	39·95
4	39·89	39·60	39·99
5	39·72	39·42	39·99
6	39·65	39·28	39·96
8	39·67	39·06	39·98
10	39·64	39·00	39·93
20			39·93

The volume of 1 drop, in the case of the 50 per cent. spirit and phenolphthalein experiments, was deliberately made very small (0·02 c.c.), whereas the size of the methyl orange drop was double this amount (0·04 c.c.).

Thus, in a sugar determination, in which half the added iodine is used up during the oxidation, a positive error of about 0·5 per cent. is introduced by one very small drop of phenolphthalein, and, with the more normal-sized drop (0·04 c.c.), a 1 per cent. error. This iodination of the indicator would explain why Slater and Acree found the iodine value higher by some 2 per cent. than the alkali value in their method, since a considerable amount of phenolphthalein appears to have been added before or during the oxidation reaction.

Methyl orange, in my experience, is free from these objections.

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NEWCASTLE-UPON-TYNE.

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE FOURTH QUARTER, 1931

OF the 1371 samples examined during the month (1292 informal and 79 formal), 66 were adulterated or incorrect.

CHALK IN SWEETS.—A formal sample of sweets contained 7·5 per cent. of chalk and 3 per cent. of talc, and consisted of a core of flavoured chocolate covered with a film of gum followed by a layer of chalk, the whole being coated with coloured sugar. The tablets were about three-eighths of an inch in diameter, and were similar in appearance to a medicinal tablet. The manufacturers were approached through the vendors, and, after some correspondence, agreed to drop the use of chalk or insoluble ingredients in the manufacture of the sweets.

FALSE LABELLING OF CONDENSED MILK.—The label of one sample of condensed full cream unsweetened milk bore the words, ". . . evaporated milk is pure, rich milk concentrated to such an extent that enables it to be substituted for cream if desired," and, again: "Can be used undiluted for tea, etc., and then becomes an excellent substitute for cream."

PARAFFIN OIL IN TURPENTINE.—Twelve informal samples of turpentine, of which six had been purchased from pharmacists and six from oil and colour merchants, were analysed. Of these, one bought at a pharmacy, was adulterated with about 25 per cent. of mineral oil. A formal sample was of similar composition. The vendor was prosecuted and fined 10s., his defence being that paraffin oil had, accidentally, been filtered into the jar containing his stock of turpentine.

H. H. BAGNALL.

COUNTY OF SOMERSET

ANNUAL REPORT OF THE COUNTY ANALYST AND BACTERIOLOGIST FOR THE YEAR 1931

THE number of samples (chemical and bacteriological) examined was 11,114, of which 1038 were taken under the Food and Drugs Act, including 19 "appeal-to-the-cow" samples. Of the 997 samples submitted by the police, 32 were adulterated.

FREEZING-POINT TEST FOR ADDED WATER IN MILK.—The test* was applied in 8 cases, with the following results:

				Appeal Sample.		
A	B	C	D	E	F	G
Solids-not-fat Per Cent.	"Presumed" added water Per Cent.	Depression of freezing point °C.	Calculated added water from C Per Cent.	Solids-not-fat Per Cent.	Added water by comparison of A with E Per Cent.	Depression of freezing point °C.
8·48	—	0·52	5·5	—	—	—
4·51	46·9	0·27	51·0	8·8	51·3	0·555
7·54	11·3	0·455	17·25	8·65	13·0	0·54
8·42	1·0	0·505	8·2	9·05 8·88 9·05	6·3	0·56 0·56 0·545
7·51	11·5	0·485	11·8	8·53 8·68	12·5	0·555 0·55
6·36	25·0	0·39	29·1			

The above results show (1) That the amount of added water calculated from the "presumptive" standard of 8·5 per cent. for solids-not-fat (Col. B) is usually considerably below the actual amount of added water, as indicated by the freezing point (Col. D).

(2) The added water calculated from the freezing point (Col. D) shows very close agreement with the added water calculated from the deficiency of the solids-not-fat below that of the Appeal Sample (Col. F).

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* The apparatus used was that described by Andrew (ANALYST, 1929, **54**, 210); the degree of super-cooling was 1° C. (not more).—D. R. W.

In each of the above cases the presence of added water was further corroborated by the demonstration of the presence of nitrates, and no nitrates were found in any of the appeal samples.

With the apparatus in use normal milk is found to give a depression of the freezing point of 0·54 to 0·56° C., with average of 0·55° C. Usually an opportunity is afforded of checking this figure with the actual normal milk of an appeal sample before reporting on the adulterated sample.

In 7 of the 470 samples of milk tested, nitrates were found. Of these 7 samples, 6 showed added water by the freezing-point test. One sample contained nitrates, and in considerable amount, without addition of water, probably due to contamination of the bottle, milk vessel or straining cloth.

COD-LIVER OIL.—Of the eight samples analysed, two contained more vitamin *A* than the average, the dilution figures (*i.e.* the limit of dilution of the oil with chloroform for the production of blue colour with the antimony chloride reagent; *cf.* Andersen and Nightingale, *J. Soc. Chem. Ind.*, 1929, **48**, 139T; ANALYST, 1929, **54**, 481) for these two samples being 3300 and 3000, the average being taken as 2000. The remaining six were below the average, the lowest giving a dilution figure of 700.

Five samples of cod-liver oil and malt extract were analysed. The cod-liver oil extracted from the mixture contained vitamin *A* in an amount represented by dilution figures ranging from 500 to 2250.

LEAD IN HOME-MADE WINE.—A sample of home-made wine was found to contain 250 parts per million of lead.

ASH FROM CREMATION.—A woman was seen scattering a white powder on Exmoor, and later a deed case was found by the police near by containing a greyish powder; this was shown to a local pathologist, who said that it looked like bone ash. The police asked for an analysis, and this showed calcium (as CaO), 42·67 per cent.; phosphoric anhydride (P_2O_5), 29·84 per cent. The alkalinity indicated about 3·0 per cent. of free calcium oxide, leaving a balance of calcium equivalent to 10 per cent. of calcium carbonate. It was only possible to say from the analyses that the result was consistent with bone ash.

DENYS R. WOOD.

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

BLOOD GROUPING IN A CASE OF DISPUTED PATERNITY

McGOVERN *v.* BRUEN

ON January 25th a case came before the Dublin Circuit Court, on appeal from the District Court, under the Illegitimate Children (Affiliation Orders) Act, 1930 (No. 17). The alleged father of the child was sixty-five years old. Evidence was given, pursuant to Section 3 (2) of the Act, to show that the man had had intimate relations with the plaintiff, the mother of the child, and that he could have had relations at about the date on which the child was conceived. For the defence, evidence was brought to show that the plaintiff had been intimate with a man other than the defendant. The District Court decided that Bruen was the father of the child, and in the Circuit Court, on appeal, fresh general evidence was brought forward, and the evidence of the blood grouping test* was given. Counsel for the plaintiff submitted that the Court could not accept such evidence as accurate or infallible, as the test had been in existence only for a short time, and it was not generally accepted. Counsel for the defendant did not ask the Court to accept the test as infallible or over-riding all other evidence, but he desired the Court to hear it, and to give it the weight it would appear to warrant. The Court decided to hear evidence concerning the test.

Dr. G. C. Dockery, M.B., Rockefeller Research Fellow, Trinity College, Dublin, testified that he had performed the test in the presence of Dr. Stephens, Clinical Pathologist, Adelaide Hospital. He deposed that he found the blood of the mother to belong to Group B, that of the alleged father to Group AB, and that of the child to Group O (RR). In his opinion, the man could not have been the father of the child; this opinion was based on his own knowledge and reading of the subject.

Dr. Stephens deposed as to the correctness of the findings. He stated that research on the test was still in progress, but that the medical profession had not universally accepted it as infallible, and that it had not been given in evidence in any Court in Great Britain or Ireland, or in America, or in France.

Dr. John McGrath, Lecturer in Medical Jurisprudence, University College, and State Pathologist, gave evidence as to the reliability of the test, and as to the fact that Bernstein's theory, though relatively recent as regards its application to human blood factors, was based on well-founded and established laws of descent, first elaborated by Mendel. He explained to the Court the manner of making the test and its significance. He believed that the theory was not accepted generally by the medical profession because its meaning and the facts supporting it were not generally known to that profession; but he considered that when it became known, with the overwhelming evidence in its favour, it would be accepted.

His Lordship allowed the appeal, deciding that the man was not the father of the child.

There was another similar case, brought under the same Act, in which the test was not eliminative, and was, therefore, of no significance whatever; nevertheless, evidence concerning it was given by Dr. McGrath and Dr. Johnson of Londonderry in the Circuit Court at Lifford, Co. Donegal, before Judge Moonan, on March 14th, 1932.

In a further case (still *sub judice*) in Dublin, the Judge has expressed his desire that the test should be carried out.

*TABLE

Parents	Offspring	
	May be	Cannot be
AB + AB	AB, A, or B	O
AB + A	"	"
AB + B	"	"
AB + O	A or B	AB or O
A + A	A or O	AB or B
A + B	AB, A, B, or O	No group impossible
A + O	A or O	AB or B
B + B	B or O	A or AB
B + O	"	"
O + O	Must be O	AB, A, or B

Cf. ANALYST, 1930, 55, 59; and Martley, ANALYST, 1928, 53, 14.

EVIDENCE ON BLOOD GROUPS IN A TRIAL FOR MURDER

REX *v.* FREEDMAN

ON March 10th, at the Central Criminal Court, before Mr. Justice Hawke, a man named Freedman was found guilty of the murder of a woman, who had been found with her throat cut on the stairs of a city office.

Dr. Roche Lynch, F.I.C. (Senior Analyst to the Home Office), stated that the outside right pocket was lightly stained with human blood, and the dust from the pocket contained rabbit fur. The safety razor blade which was mounted in a holder, and had been found pushed down behind the seat of an omnibus which passed close to the scene of the murder, was stained with human blood, and this blood belonged to Group I. Attached to the razor by dried blood were some rabbit hairs. Examination of the deceased's fur necklet showed that it was stained with human blood of Group I. The necklet was made of artificial fur, and contained no rabbit hairs, but a pair of gloves found in the possession of the prisoner at the time of arrest were lined with rabbit fur. Of the four groups into which human blood could be divided, Group I was characteristic of 3 per cent. of the population; Group II of about 45 per cent.; Group III of about 10 per cent.; and Group IV of about 42 per cent.

The submission of the prosecution was that the fact that the blood on the razor belonged to the rarest of the groups, and that it was of the same group as the blood of the murdered girl, linked up the weapon with the crime. In addition, it was submitted that after the murder the accused had placed the razor in the pocket of his coat, that the lining thereby became stained, and at the same time the rabbit hairs which, it was suggested, had come originally from the gloves, had become attached to the blood, which had not yet dried, and that the razor was not deposited on the bus until some time after. Incidentally, it may be noted that the bus conductor identified the prisoner as a man who had travelled on the bus on the morning of the murder.

Department of Scientific and Industrial Research

THE INVESTIGATION OF ATMOSPHERIC POLLUTION

REPORT OF OBSERVATIONS IN THE YEAR ENDING 31ST MARCH, 1931 (SEVENTEENTH REPORT)*

THE Report, the general arrangement of which is similar to that for 1930 (ANALYST, 1931, **56**, 254), includes, for the first time, the report made by the Standing Conference to the co-operating bodies on its work during the year, together with an account of the work of the Research Committee.

REPORT OF THE ATMOSPHERIC POLLUTION RESEARCH COMMITTEE

(1) SULPHUR GASES IN AIR.—The development of a method for the routine determination of sulphur in the air has been completed, and a description issued to the co-operating bodies. The details are embodied in *Appendix I* (pp. 38–49) of the present volume. The method consists in passing a known volume of air through a

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* Published Feb. 1, 1932, pp. 110. Obtainable from H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 5s. 6d. net.

solution of hydrogen peroxide, and determining by titration the amount of sulphur dioxide absorbed.

(2) MEASUREMENT OF DAYLIGHT.—The apparatus devised by the National Physical Laboratory for the measurement of daylight is to be submitted to independent trial by members of the Research Committee. Light taken from the whole of the sky is passed through an optical wedge in contact with an opaque metal plate perforated with a series of small holes in a line, the intensity of the light transmitted varying from one end to the other with the varying density of the wedge from point to point. Two images of the row of holes are formed on photographic paper by means of a split lens, and, by placing suitable filters over the corresponding halves of the lens, the radiation forming one image is confined to the ultra-violet part of the spectrum, and that forming the other image to the invisible spectrum. By noting the last hole of each series visible in the developed print an arbitrary measure of the relative intensity of the two kinds of radiation during the period of exposure is obtained.

(3) The data obtained from the Owens Jet Dust Committee have been completed, and a report is under consideration.

(4) The National Physical Laboratory has continued work on the determination of water in fog.

(5) SPREAD OF POLLUTION IN AIR.—The investigation on the spread of pollution at Norwich under different weather conditions has been completed, and results are incorporated in *Appendix II* (pp. 50–58). The pollution is measurable up to a distance of 5 or 6 miles from the city by the Owens Jet Dust Counter, and the band of pollution is some miles wide at its broadest part, tapering off as the distance from the town increases. The amount of pollution was found to fall off inversely with the distance from the centre, and from these figures the probable effects of pollution from larger cities have been calculated.

(6) Two investigations added to the programme are the measurement of smoke intensity, and the possibility of devising means of distinguishing from one another grits emitted by different types of furnace.

(7) The method suggested for preventing the bursting of the bottles of the deposit gauges during prolonged frost consists in the insertion of a rubber bag, the collapse of which under pressure should ease the stress.

RECORD OF OBSERVATIONS.—During the year 14 new gauges and 3 new automatic filters were installed, so that, in all, 98 deposit gauges and 14 automatic filters were in operation. The monthly deposit figures are now recorded in English units, as well as metric tons per sq. km., the latter being given below. The maximum and minimum monthly deposits were:—*Tar*: Walsall, 55; Kingston-upon-Hull, 2; *other insoluble carbonaceous matter*: Burnley, Town Hall No. 2, 363; Birmingham, West Heath, 31; *ash of insoluble matter*: Birmingham Central, 674; Garston, near Walford, 65; *ash of insoluble matter*: London, Ravenscourt Park, 730; Leicester, 61; *total solids*: Burnley, Town Hall No. 2, 1794; Leicester, 236; *rainfall*: Rochdale, Electricity Works, 111 mm.; London, South Kensington, 41. About two-thirds of the stations show reduction in the amount of impurity deposited; and one-third, an increase or no improvement. The most remarkable improvement is for sulphates, mainly produced by combustion. The abnormal deposit of chlorides for the Southport, Marshside, gauge is shown to be due to sea-salt, and, with wind blowing off the sea and the air dry, the water may be evaporated from the salt particles, which may then appear as a white haze, and considerable deposits of salt may occur. At certain stations the *p*H values of the deposit have been measured. If it be assumed that the acidity due to the carbonic acid of the air corresponds with a *p*H not lower than 5·5, more than half the stations indicate an acid collection during December, January, and February, whilst one-third or less were acid in May, June and July. The collections at Bourneville and Cardiff were never acid, at Edinburgh seldom so, and at Liverpool, Rochdale, Salford, and Wakefield usually so. The nature of the acid remains to be determined, the figures for total sulphates not confirming the view that it is mainly sulphuric acid.

MEASUREMENT OF DEPOSIT BY EXPOSING GLASS PLATES.—Professor Cohen's method of exposing glass plates to the air for some time, washing in water and determining their opacity, which is mainly designed for measuring the amount of tarry soot, though not regarded as very likely to provide useful information, is to be tried at about 3 typical stations by exposing the plates in the same position as the deposit gauges and comparing the results.

AUTOMATIC FILTER.—As a result of tests before a continuously open window, in the open, and in closed rooms, the particles are regarded as being in such a finely divided state, and settling so slowly, that apparently they travel with air wherever it goes. A new type of automatic filter has been evolved, operated by means of a weight moving through gearing, the aspiration being done by a collapsible rubber bellows with a reciprocal motion by means of a crank and connecting rod, thus making the apparatus independent of any other source of energy, and also providing for the filtration of 2, 4 or 8 litres of air instead of a fixed 2. A special measurement of soot particles in smoke fogs in London shows that there is no improvement compared with the condition in 1922.

Appendix III deals with atmospheric deposits at Cheltenham, and the General Deposit Tables occupy the last 50 pages.

D. G. H.

Fiji

ANNUAL REPORT OF THE GOVERNMENT CHEMIST FOR THE YEAR 1930

THE Report of the Government Chemist for Fiji (Mr. W. J. Blackie) forms part of the Annual Report of the Department of Agriculture, although his work also includes analyses made for the Constabulary, Municipal Council, Medical Department, Customs, and private persons. The total number of analyses made in 930 was 735.

MILK.—Mr. Blackie was appointed at the end of November, 1929, and during the last five weeks of that year examined 22 samples for the Municipal Council. Twenty-one of these were adulterated with water, many grossly so, and almost all contained animal hair and dirt. The offenders were drastically punished, with the result that the quality of the milk improved to such an extent that, in 1930, it conformed generally to the pure food standards (fat, 3·2 per cent.; solids-not-fat, 8·5 per cent.).

GHEE.—Twelve samples of ghee were examined for purity. All of these were adulterated, some with mutton tallow, others with hydrogenated fats, and some of the local material with coconut oil.

CONSTABULARY.—The work for this Department covered a fairly wide field, and included the examination of smoking utensils and prepared products for opium and gunjah; determination of alcoholic contents of hop beers and liquors of various kinds; determination of the nature of liquors; examination of articles for bloodstains.

Hop Beers.—Practically all of the hop beers submitted contained more than the allowable 2 per cent. of alcohol. Some of the figures obtained were as high as 7 per cent. Many of these hop beers are unfit for human consumption.

An interesting feature of the work for this Department is the increased use that is being made of a scientifically equipped laboratory as an aid in the elucidation of crime. The importance of this is displayed more particularly by the two following cases. In one case it was shown from the examination of a garden fork, piece of shirt, skin and flesh from the back, an axe, and a portion of a skull that the crime could be connected with the axe and fork which had been originally submitted for the determination of blood stains. In another case the examination of a shirt and the perforations it contained showed that a fatal shot had been fired from a gun held at a greater distance from the target than alleged by the accused.

Toxicological Analyses.—Ten of 14 samples examined were in connection with the deaths of two Europeans. Mention must be made of the haphazard methods usually adopted in submitting toxicological specimens for chemical examination. Glass-stoppered jars are not used, and almost invariably it has been necessary to ask for liver and other organs, in addition to the stomach contents. Also, very little information generally derived from a post-mortem is given. A toxicological examination, even where a definite type of poison is suggested from the post-mortem, involves a considerable amount of detailed work, and a complete examination should very seldom be required. In all the human cases so far submitted it has been necessary to make a complete examination, involving in each case a fortnight to three weeks of concentrated work. Such an examination is seldom required in other countries where considerable information is derived from the post-mortem.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Sheep's Milk. F. Diacon. (*Ann. Falsificat.*, 1931, **24**, 594–596.)—The milk of sheep is frequently adulterated with that of cows or goats, and, in order to distinguish the milks, the proportion of chlorides (as sodium chloride) becomes important. The milk of Swiss cows contains about 0·18, and that of Dutch cows about 0·191 per cent. of chloride, and that of sheep about 0·165 per cent., whilst goat's milk is richer in chlorides than cow's milk. Sheep's milk, adulterated with goat's milk, will show low values for casein and fat and a high value for chlorides, whilst adulteration with cow's milk will result in casein and fat being low, but the value for chlorides will remain about normal, or be slightly higher if Dutch cows are concerned. Average values for the milk of 48 sheep, as published by Martin (*Ann. Falsificat.*, 1928, **21**, 236), are:

	Total Solids Per Cent.	Fat Per Cent.	Casein Per Cent.	Lactose Per Cent.	Chlorides Per Cent.
Morning ..	22·66	9·46	7·05	4·87	0·171
Evening ..	21·85	8·61	7·11	4·94	0·159
Average ..	22·55	9·03	7·08	4·90	0·165

D. G. H.

Action of Heat on Tomato Conserve. O. Carrasco and E. Sartori. (*Ann. Falsificat.*, 1931, **24**, 589–594.)—Tomato conserves, when heated, undergo alterations which depend largely on their concentration. Carbon dioxide is liberated in direct proportion to the concentration, the temperature (between 100° and 110° C.), the time, and the quantity of sugars present, but, even after 6 hours' heating, it was not possible to reach equilibrium, owing to the difficulty of getting the heat to penetrate the whole mass of material. Sixteen grms. of a conserve, consisting of 73 per cent. of dry material, were heated to 100° C., and in 6 hours about 1·41 per cent. of carbon dioxide (on the dry material) had been liberated. On steam distillation the liquid collected gave reactions indicating the presence of oxymethyl-furfural, and when this was distilled in the presence of hydrochloric acid the reactions for furfural were obtained. There is little doubt that a moderate temperature is sufficient to allow the weak organic acids to react with the hexoses, dehydrating them and eliminating carbon dioxide to the point of formation of furfural derivatives and formic, laevulinic and humic acids. It was found that in the absence of sugars very little decomposition occurs. Although the figures obtained by drying *in vacuo* cannot be regarded as absolute, yet it is evident that the dry substance cannot be determined by heating at 100° C., and, still less, at 105° C., particularly in the case of highly concentrated products.

D. G. H.

Loss of Glucose from Dried Peas on Soaking. W. M. Clifford. (*Biochem. J.*, 1931, **25**, 1999–2003.)—The common treatment of dried peas when used as human food is prolonged soaking, so that they may imbibe water, followed by boiling. This procedure is thought by some to cause loss of protein, mineral matter and carbohydrates, and thus to cause a decided drop in the food value of the peas. Masters (*Biochem. J.*, 1918, **12** 231) investigated the loss incurred by beans on soaking, and found that 100 grms., soaked in 250 c.c. tap or distilled water, lost 1·5 to 2·2 per cent. solids, and, of this, a considerable proportion consisted of nitrogenous extractives and salts. Similar experiments carried out with peas, with regard to the loss of carbohydrate, give the following results:—(1) Dried peas, on soaking in distilled water for 18 to 24 hours, lose 0·1 to 0·15 per cent. glucose, *i.e.* about 0·2 per cent. of their total carbohydrate. (2) This loss is unaltered by the addition of alkalis to the soaking fluid. (3) The addition of acids causes a marked rise in loss of glucose. (4) This glucose loss is more marked with organic acids than with inorganic acids. (5) The uptake of water by dried peas is depressed by the addition of acids, alkalis or salts to the soaking fluid. (6) The rate of cooking of peas is unaltered by previously soaking them in acids, alkalis, or salts, unless the concentration of alkali or salt is high enough to soften the whole pea in the cold (this would render the pea inedible). It, therefore, appears that, so far as carbohydrate loss is concerned, it is immaterial whether peas are soaked in hard or soft water. Further, the addition of the customary "pinch" of bicarbonate does not alter this slight loss or accelerate the cooking of the soaked peas. Its only effect is the usual attainment of a bright green colour by the peas soaked in a weak solution of alkali. It is shown that glucose removal is not solely a matter of permeability; the increase in glucose with acids is probably due to the liberation of glucose from some pre-formed combination in the plant cells. Any increase of ionic concentration reduces the water imbibed by dried peas. P. H. P.

Monascin, a Colouring Matter from "Red" Rice. H. Salomon and P. Karrer. (*Helv. Chim. Acta*, 1932, **15**, 18–22.)—"Red" rice, prepared in Eastern Asia by growing a mould known as *Monascus purpureus* (Wentii) on rice, contains a red colouring matter, which is used for colouring foodstuffs and beverages. The colour is due to the presence of various compounds, and one of these, named *monascin*, which has a deep yellow colour, has now been isolated in the pure state. It crystallises in long plates which sinter at about 130° C., and melt at temperatures varying, according to the rapidity of the heating, between 135° and 140° C. In water it is virtually insoluble, but it dissolves in alcohol to give a neutral solution. Elementary analysis and molecular weight determinations give results agreeing best with the formula $C_{24}H_{30}O_6$, but the molecular weight found is somewhat unreliable, as monascin readily undergoes change in solution, although in the crystalline form it appears perfectly stable. A number of reactions of monascin have been studied, but these have failed to give any indications concerning its chemical character, beyond showing that the structure is largely aliphatic.

T. H. P.

Determination of Sucrose in Beer. II. J. Fiehe. (*Z. Unters. Lebensm.*, 1932, **63**, 69–72.)—For qualitative work the beer is first decolorised with animal charcoal and filtered, and 1 c.c. of the clear filtrate is heated with 1 c.c. of concentrated hydrochloric acid on the water-bath for 1 minute. The mixture is cooled, and, on addition of 8 c.c. of a solution of phloroglucinol, the presence of sucrose is shown by a deep yellow colour changing during 1 minute through orange and red, and depositing eventually a dark brown to black precipitate; beer, free from sucrose, remains unchanged. For quantitative work, Fiehe and Kordatzki's modification of Troje's method for honey (ANALYST, 1929, **54**, 108, 241, and, especially, 748) is used. The beer (25 c.c.) is warmed with 10 c.c. of 5 *N* hydrochloric acid on the water-bath for 30 minutes, and, after dilution to 50 c.c., 5 c.c. are used directly for the determination (*loc. cit.*), the preliminary extraction with ether being unnecessary. The factor 3·5 converts the weight of hydroxymethylfurfural phloroglucide (which should be about 11 mgrms.) into sucrose, and tests on 1 to 5 per cent. solutions of sucrose gave results with an error of −0·17 to +0·14 per cent. The method was also tested on various types of beer (mainly sweet beers and Munich varieties), and on worts, both in the presence and absence of added sucrose, and gave satisfactory results. Omission of decolorisation with charcoal, and the presence of furfural (which also yields a precipitate) cause the results to be high. The factor 1·9 converts the weight of the precipitate obtained from 25 to 50 mgrms. of laevulose into sucrose. Arabinose, dextrose, maltose, lactose, and starch give no furfural or hydroxymethyl-furfural on treatment with acid under the above conditions, and do not interfere. J. G.

Extraction of Trigonelline from Raw Coffee. F. E. Nottbohm and F. Mayer. (*Z. Unters. Lebensm.*, 1932, **63**, 47–51.)—The authors' method (ANALYST, 1931, **56**, 405, 543) is modified to deal with larger quantities of coffee (*e.g.* 250 grms.), and to ensure complete removal of the sugars. The raw coffee is extracted with 750 c.c. of water for 1 hour on the water-bath, and the extract is cleared (in 2 separate portions) with 100 c.c. of lead acetate solution, the excess of which is removed. The resulting filtrate is then evaporated to 200 c.c., and the caffeine is removed by extraction with chloroform, any dissolved solvent being expelled by evaporation. The sugars are then destroyed by treating 100 c.c. of liquid with 25 c.c. of hydrochloric acid (sp. gr. 1·124) in an autoclave for 1 hour at 4·5 atmospheres, and the filtrate from the resulting mixture may then be treated with animal charcoal, and the final clear liquid evaporated in a vacuum to a syrup (*cf.* Heiduschka, *J. prakt. Chem.*, 1931, **130**, 11). Trigonelline hydrochloride is then extracted with three 50 c.c.-portions of hot alcohol, the combined extracts are evaporated, and the residue is extracted with water, again treated, if necessary, with animal charcoal, and the trigonelline is determined iodimetrically (*loc. cit.*); 0·43 per cent. was found in raw "Santos" coffee. It is suggested that a similar procedure might be used for betaine and choline. J. G.

Determination of the Sulphur Content of Ammonium Ichthosulphonate (Ichthamol). N. L. Allport. (*Quart. J. Pharm.*, 1931, 4, 566–569.)—*Inorganic sulphate* in ammonium ichthosulphonate (the ammoniated salts of the product obtained by sulphonating the sulphur-containing oil resulting from the destructive distillation of a bituminous schist) may be determined by dissolving 2 grms. of the product in 100 c.c. of cold water, adding 80 c.c. of a 2·5 per cent. solution of cupric chloride, and making up the volume with cold water to 200 c.c. After shaking and filtering, 100 c.c. of the clear filtrate are acidified with hydrochloric acid, and precipitated in the usual way with barium chloride. Results obtained by this process agreed well with those found by the ether-alcohol process. The *total sulphur* is found by mixing about 0·5 grm. of the ammonium ichthosulphonate in a porcelain crucible with 4 grms. of anhydrous sodium carbonate and 3 c.c. of chloroform, and stirring the warmed mixture continuously until all the chloroform has evaporated. To the remaining dry brown powder, 10 grms. of coarsely-powdered copper nitrate, $Cu(NO_3)_2.3H_2O$, are added, and, after thorough mixing, gentle heat is applied, which is increased when the initial reaction has subsided, until most of the material has blackened. After cooling, 20 c.c. of concentrated hydrochloric acid are added to the contents of the crucible, which has been placed in a large beaker, and the mixture is then boiled with 100 c.c. of water until the copper oxide has dissolved. After filtering (if necessary) the solution is diluted to 400 c.c. and precipitated with barium chloride. Results compared very favourably with those obtained by sodium peroxide fusion. D. G. H.

Test for the Purity of Veronal. C. G. Van Arkel. (*Pharm. Weekblad*, 1932, 69, 86–87.)—The Dutch Pharmacopoeia states that a solution of diethyl-barbituric acid (veronal) in alkali should remain bright on addition of bromine water, whilst phenyl-ethyl-barbituric acid (luminal) gives immediately a white crystalline precipitate. The test is criticised on the grounds that veronal on prolonged standing also gives a white crystalline precipitate with m.pt. 152° C. and bromine content (by micro-Carius method) 43·8, compared with 163° C., and 30·4 per cent. for the luminal derivatives, respectively. Further, in the presence of too much alkali a precipitate is immediately produced on addition of bromine water to veronal, and the presence of hydrobromic acid in the bromine water is also objectionable. It is, therefore, proposed that 8 c.c. of a fresh saturated solution of bromine water should be added to a solution of 100 mgrms. of sample in 2 c.c. of 1·1 per cent. sodium hydroxide solution, when a precipitate is at once produced from luminal, whilst the precipitate from veronal appears on standing. The test, however, is of little value, since luminal is dearer than veronal, and is, therefore, an unlikely adulterant, and the m.pts. provide better means of identification. J. G.

Solubility of Beeswax. J. J. Deeney. (*Amer. J. Pharm.*, 1932, **104**, 19–21.)—The U.S.P. states: "It (beeswax) is completely soluble in chloroform, ether, and in fixed and volatile oils; partly soluble in cold benzene and carbon disulphide, and completely soluble in these liquids at about 30° C.," but solubility tests carried out by two methods did not confirm this. Method I consisted in bringing a weighed amount of solvent to 25° C. in test tubes, 24 × 200 mm., and adding a weighed amount of wax in very small pieces. The corked test tubes were kept in a water-bath at 25° C., shaken at frequent intervals, and solubility observations were made over two days. Method II.—The solvent was weighed in 250 c.c. round-bottomed flasks, the weighed beeswax added, and the flasks heated under reflux condensers until the wax was just completely dissolved. On cooling, the wax solutions were poured into test tubes and the congealing points noted. Subsequent tests were then made, and the ratio of wax to solvent determined with which the wax would remain completely dissolved at 25° C., but would congeal at 24° C. By Method I, beeswax was found to be soluble in chloroform, carbon tetrachloride, benzene, and carbon disulphide; sparingly soluble in petroleum spirit and oil of turpentine, and insoluble in acetone and fixed oils. By Method II it was freely soluble in the first four solvents, soluble in petroleum spirit and oil of turpentine, and very slightly soluble in acetone and fixed oils. It is not advisable to state the solubility figures of beeswax in volatile oils, as these differ with the composition of the oils. The solubility figures obtained are tabulated.
D. G. H.

Biochemical

Body Fats of the Pig. I. Influence of Ingested Fat on the Component Fatty Acids. R. Bhattacharya and T. P. Hilditch. (*Biochem. J.*, 1931, **25**, 1954–1964.)—The component fatty acids of the perinephric fats and the outer and inner layers of the back fats from pigs fed on a basic diet (i) alone or supplemented by 3 per cent. of (ii) shea butter (a solid fat), or (iii) arachis oil (a liquid fat), have been determined. The general relationships which were recently observed among the various classes of fatty acids of tallows are found to be present also in the pig body fats, more especially a tendency to approximate constancy in the molar content of C_{18} acids in spite of variation in the total proportion of saturated to unsaturated acids; increase in saturation in the pig fats is produced mainly by increase of stearic acid, and corresponding diminution in oleic acid. These views accord, in general, with those at which Ellis and his co-workers have arrived in the course of their recent studies on soft pork. The composition of the outer layer of back fat differed in each case from that of the inner layer, the latter being intermediate in type between the former and the perinephric fat, which it more closely resembled. The outer layer of back fat was the most unsaturated, but the differences between the three depôt fats were much reduced when the diet of the animals included arachis oil. As regards the influence of ingested fat in the diet, the body fats from animals whose feed included the relatively saturated shea butter were not greatly different from those of the control-fed animals, but presence of arachis oil in the diet led definitely to increase of unsaturation in the stored fat, and also to increase in the proportion of linolic acid in the unsaturated acids. Consideration of the experimental data, in conjunction with the results of Ellis and collaborators, on the feeding of pigs with rations containing high proportions of vegetable fat, confirms the previous conclusions of the authors as to the general rules which govern the composition of depôt fat of animals fed on a balanced diet, and shows clearly the amount of added fat (beyond about 5 to 8 per cent. of the diet) which leads to the breakdown of these characteristics. The data, as a whole, prove that much of the normal depôt fat of the pig must be derived by synthesis in the animal from carbohydrate or other non-fatty part of the feed, rather than by direct assimilation of fat. This deduction appears to be of, at least, equal importance, as regards the normal animal metabolic processes, to the more obvious one that, with an excessive fatty diet deficient in carbohydrates, etc., the pig is capable of utilising directly much of the ingested fats for storage. P. H. P.

Basic Amino-Acids of Wool. A. M. Stewart and C. Rimington. (*Biochem. J.*, 1931, **25**, 2189–2192.)—Only two determinations have been made of the basic amino-acids present in wool. Marston (*Council Sci. and Ind. Research, Commonwealth of Australia, Bull.*, 1928, 38) used the indirect Van Slyke method, and found a constant proportion of basic nitrogen in several samples of wool analysed. His figures for histidine, arginine and lysine were 6·9, 10·2 and 2·8 per cent. respectively. Vickery and Block (*J. Biol. Chem.*, 1930, **86**, 107), in a careful series of determinations by direct isolation from a sample of wool, found 7·8 per cent. of arginine, 2·3 per cent. of lysine, and only 0·66 per cent. of histidine. They commented upon the fact that other keratins, such as human hair, have been found to contain 0·5 per cent. of histidine, whereas Marston's figures are over 10 times as great. The basic amino-acids in a single sample of wool (a fleece of Australian wool) have now been determined by the method of Calvery (*J. Biol. Chem.*, **1929**, **83**, **631**). The values for histidine have been verified by the colorimetric method of Hanke and Koessler (*J. Biol. Chem.*, 1920, **43**, 527; ANALYST, 1920, **45**, 454). This wool gave 0·55 per cent. histidine, 6 per cent. arginine and 2·2 per cent. lysine. These figures are in agreement with those given by Vickery and his co-workers for wool and for human hair, and support his opinion "that Marston has been led to an erroneous conclusion with respect to the proportion of histidine yielded by wool." No claim is made that the proportions of the basic amino-acids present do not vary from wool to wool, but it is clear that the percentage of histidine is of the order found by Vickery and Block, namely, 0·5 to 0·6 per cent.

P. H. P.

Wax Constituents of the Apple Cuticle. A. C. Chibnall, S. H. Piper, A. Pollard, J. A. B. Smith, and E. F. Williams. (*Biochem. J.*, 1931, **25**, 2095–2110.)—As a preliminary to work on the chemical constitution of leaf waxes of various forage grasses, the wax fraction obtained from apple peel (a material which can readily be obtained in quantity) has been used to elaborate methods for the separation of the paraffins, ketones, primary alcohols and secondary alcohols which occur in many plant waxes. The method of separation adopted is based on the solubility in ether and alcohol of the sodium salts of the secondary alcohol phthalates. The following is a brief outline of the method:—The crude plant wax is first saponified to break down any true wax esters, and the unsaponifiable material is then removed and heated for 18 hours with phthalic anhydride, to convert all the alcohols present into hydrogen phthalates. Excess of phthalic anhydride is then removed, and the mixed phthalates, together with any unchanged material, dissolved in ether. The ethereal solution is gently shaken with a slightly warm aqueous solution of sodium carbonate. The sodium salts of the primary phthalates are precipitated, and can be quantitatively separated by appropriate treatment. The ethereal solution, which now contains the sodium salts of the secondary phthalates, and perhaps ketones and paraffins, is evaporated to dryness and taken up in a relatively small volume of boiling alcohol. On cooling, the paraffins and ketones crystallise out quantitatively, leaving in the mother-liquor the very soluble sodium salts of the secondary alcohol esters. The mixture of paraffins and ketones can then be separated by the method of Channon and Chibnall (*Biochem. J.*, 1929, **23**, 168), in which the ketone is converted into its oxime, and advantage is taken of the greater solubility of this oxime in solvents such as petroleum spirit and mixed ether and acetone. This relatively simple procedure separates at once the primary alcohols, the secondary alcohols, ketones and paraffins into four distinct fractions, each of which can be readily purified. In practice, certain modifications are essential. A second treatment with phthalic anhydride for 18 hours is necessary to ensure that all the alcohols have been converted into their hydrogen phthalates, and it is advantageous to remove hydrocarbons before treatment with phthalic anhydride. The products are subjected to *X*-ray analysis; their melting points, transition-points and crystal spacings are considered. The following constituents of apple peel wax have been definitely identified: *n*-nonacosane, *n*-heptacosane, *d*-10-nonacosanol, *n*-hexacosanol, *n*-octacosanol and *n*-triacontanol. No ketone was found. The bearing of these findings on the metabolism of paraffins in the plant is discussed. P. H. P.

Oil Development in the Seed of a Growing Plant. J. V. Eyre. (*Biochem. J.*, 1931, **25**, 1902–1908.)—A study has been made of changes which take place in the rate of formation and in the character of the oil in the seed of flax—*Linum usitatissimum* and *L. cribrosum*—throughout its development and ripening periods. The results were obtained during a study of the so-called "quality" of fibre for spinning and the "quality" of seeds for special purposes. Observations show that, in oil formation, the acidic constituents are formed first. Whether the glycerol is formed at the same time, only combining with the fatty acid at a later stage, or whether the formation of glycerol itself is delayed, is not clear. The observations reveal a remarkably rapid oil formation over a period of some 15 days, during which a maximum of about 36 per cent. of oil, calculated on the dry weight of the seeds, is reached. The oil formation ceases with the disappearance of chlorophyll, about 21 days from the time of flowering. The colour of the linseed oil extracted at various stages of development and ripeness of the seed was noted. At first the oil was more than usually viscous, and was of a greenish hue, but this gave place to a greater mobility and the characteristic full golden yellow colour as the age of the seed advanced; further, the oil became increasingly lighter in colour, until, after 53 days from flowering, the seed yielded a very pale yellow oil; and, when the harvested plants themselves, or merely the capsules containing the seeds, were stored under cover, indoors, the oil extracted from the seed was practically colourless. Changes in the nature of the oil continue after oil formation has ceased; its degree of unsaturation, as measured by its iodine absorption, continues to increase, and, therefore, in flax, oil from fully mature seed is of greater value as a drying oil than is oil from less mature seed. It is pointed out that this increase in the degree of unsaturation is apparently an entirely separate change, independent of oil formation. A point of interest is that, whereas, during the early stages, a reducing system must prevail in order to account for the formation of acids from carbohydrates, this must change to an oxidising system, leading to the formation of unsaturated acids. P. H. P.

Chemical Composition of the Spores of the Higher Fungi. W. Friese. (*Z. Unters. Lebensm.*, 1932, **63**, 72–77.)—The spores (15 varieties) were carefully separated, washed, and dried in air, and gave the following percentage values (minimum, maximum and mean, respectively):—Dry substance (at 102 to 105° C.), 86·75, 97·63, 94·81; ash, 1·51, 5·29, 2·99; iron, 0·020, 0·054, 0·037; manganese, 0·001, 0·003, 0·002; Kjeldahl nitrogen (6 varieties), 2·18, 4·30, 3·67; fat soluble in ether (2 varieties), 3·03, 3·88 (n_D^{40}, 1·4812, 1·4743, respectively). The four *Amanita* varieties investigated had ash-contents of 1·55 to 2·14 (mean 1·90) per cent. on the oven-dried spores, whilst the corresponding figure for the remaining varieties was 3·48 per cent. The percentage compositions of the ash of a potato mould and its spores (cf. *id.*, 1929, **57**, 607) were found to be, respectively:—K_2O, 48·35, 52·77; Na_2O, 2·35, 4·48; CaO, 1·18, 0·004; MgO, 1·30, 0·001; Fe_2O_3, 0·30, 1·306; Mn_2O_3, 0·04, 0·090; Al_2O_3, 1·79, —; P_2O_5, 24·78, 34·27; SO_3, 4·09, 0·466; Cl′, 6·35, 2·54; SiO_2, 6·52, 2·95. In general, the washed air-dried spores contained less ash and water and more iron and manganese than the corresponding air-dried fungi from which they were derived, the differences being most marked in the cases of the ash and iron contents of the *Amanita*. J. G.

Determination of Aluminium in Certain Aluminium Protein Compounds. C. G. Pope. (*Biochem. J.*, 1931, **25**, 1949–1953.)—In connection with work on the precipitation of diphtheria toxoid by various aluminium salts it became necessary to make a number of determinations of the aluminium content of the precipitates so formed. Berg (*Chem. Ztg.*, 1926, **50**, 754) used 8-hydroxyquinoline for the determination of aluminium, and, later, Pichler [*Mikrochemie* (*Festschrift*), 1929, **6**; ANALYST, 1930, **55**, 298] reported a micro-method based on its use. A method is now described suitable for the determination of amounts of aluminium between 0·3 and 1·0 mgrm. present in suspensions produced by the addition of potassium alum or other aluminium salts to *C. diphtheriae* culture filtrates; it depends on the precipitation of the aluminium with 8-hydroxyquinoline and the determination of the amount of the latter contained in the precipitate. A difficulty was encountered in dealing with the aluminium complex salt, owing to the fact that the precipitate is not easily "wetted," and behaves rather like finely divided sulphur. The addition of a few drops of 10 per cent. sodium taurocholate proved effective in overcoming this difficulty. It was found more convenient to determine the amount of "complex" formed volumetrically instead of gravimetrically. Berg titrated the complex directly with standard bromine solution and the use of an indicator, but the author obtained better results when the complex was dissolved in hydrochloric acid, excess of potassium bromate added, and the excess bromine determined by the addition of potassium iodide and titration with thiosulphate. Borax solution was found to be much more satisfactory than the ammonium acetate recommended by Pichler to precipitate the complex; it also dissolved the alum-toxoid precipitates and so obviated the necessity for incineration with sulphuric acid, and was used to wash the precipitate on the Gooch crucible to remove excess 8-hydroxyquinoline. The reagents required and the method of determination are described in detail. It is shown that the presence of organic materials (*C. diphtheriae* culture filtrates) does not affect the results, and the method is suitable for the special purpose for which it was devised.

P. H. P.

Vitamin *A* and Carotene. VIII. High Potency Vitamin *A* Concentrates. T. Moore. (*Biochem. J.*, 1931, **25**, 2131–2135.)—Vitamin *A* concentrates prepared from the liver oils of rats and pigs which had received diets containing large amounts of carotene, as red palm oil, were compared with concentrates derived from turbot liver and sole liver oils. The methods employed in the concentration of the vitamin were the same in all cases. Although the initial blue values of the oils varied widely, little difference could be detected in the activities of the final concentrates, which approached an average value of 2400 B.U. per mgrm. (Pharmacopoeia colour value, 45,000) in the antimony trichloride test, corresponding with a minimal dose of about 0·001 mgrm. in rat growth experiments. These results suggest either that the concentrates must have consisted substantially of actual vitamin *A*, or, alternatively, that the vitamin must have been associated with other substances of similar solubility properties in remarkably constant proportion. A comparison of the biological activity of the most active concentrates with carotene in parallel experiments is now in progress. P. H. P.

Reduction-Capacity of Plant Foodstuffs and its Relation to Vitamin *C*. I. Reducing Substance in Lemon Juices. J. Tillmans, P. Hirsch and W. Hirsch. (*Z. Unters. Lebensm.*, 1932, **63**, 1–21.)—Juice was expressed from a large number of lemons in apparatus free from metals (*e.g.* copper) likely to exert catalytic effects in small traces, and was treated with sufficient 2 *N* sulphuric acid to liberate all the organic acids. Calcium carbonate (65 grms. to 1 litre of juice) was then added, in small quantities at a time, and the carbon dioxide was removed in a stream of nitrogen until the reaction was neutral to litmus. The liquid (about 10 litres) was then decanted from the solid portion, and 4 c.c. of 25 per cent. phosphoric acid were added. As a result of preliminary experiments with numerous solvents and inorganic precipitants the procedure finally adopted was to evaporate the solution to 2 litres and to shake the resulting liquid with a 4-fold volume of acetone, and, after 16 hours at 0° C., to remove the solvent by distillation in carbon dioxide; these operations were repeated 5 times, in the last instance, after evaporation of the juice to 20 c.c. The resulting crystalline precipitates were collected and re-precipitated with acetone from a solution in methyl alcohol and water, and stored in nitrogen at 0° C. A solution of the solid was then neutralised with a solution of barium hydroxide in methyl alcohol, and 2 *N* sulphuric acid was added, followed by 75 c.c. of 10 per cent. lead acetate solution, the excess of which was removed by precipitation with hydrogen sulphide, any residual gas being expelled by boiling under reduced pressure. The solution was finally extracted with ether for 6 hours, the residue left on evaporation of the resulting liquid was extracted with acetone, which was then removed by evaporation, and a solution of the residue in water was used for subsequent experiments. The principal stages of the process were controlled by titration of the reduction-capacity with 2·6-dichlorophenol indophenol as indicator (*cf.* ANALYST, 1929, 54, 176). This dyestuff, which changes from red to violet between *p*H 4 and 5, is blue at *p*H 7. The usual procedure was followed (*loc. cit.*), a slightly acid solution of the dye (to litmus) being added to the solution under investigation until a blue colour permanent for 1 minute was obtained. The solution was standardised against 0·01 *N* titanous chloride solution by addition of the latter to 20 c.c. of the former, containing a drop of dilute acetic acid and sufficient sodium acetate just to produce a blue colour which is destroyed by the titanium solution at the end-point. The titanous chloride was standardised against ferric ammonium sulphate in the usual way (Knecht and Hibbert). Standardisation of the indicator directly against the iron salt may also be used, but appears to be less satisfactory. The final purified preparation from the lemon juice was thus found to have an "apparent equivalent weight" of 500 (*e.g.* 10 mgrms. of dry substance, requiring 10 c.c. of 0·001 *N* indicator solution corresponds with an "apparent equivalent weight" of 1000). The preparation was slightly acidic, soluble in acetone, water or in methyl or ethyl alcohols, but insoluble in chloroform, benzene or ether, and gave a pale-blue colour in ultra-violet light similar to that from the original juice. The Molisch carbohydrate reaction was strongly positive, but the phenol and tannin tests were negative (*cf.* Agopian and Bezssonoff, *Eng. Pat.*, 1921, 168,903; *French Pat.*, 1925, 595,537; Rygh, Rygh and Laland, ANALYST, 1932, 57, March issue; Zilva, *id.*). The substance contained a little nitrogen, and gave a positive xanthoprotein reaction, but other protein reactions (ninhydrin, biuret and precipitation tests) were negative. Biological experiments on guinea-pigs indicated an appreciable antiscorbutic power in a daily dose of the preparation corresponding with 1 c.c. of fresh juice, but both the juice and preparation lose this power after oxidation by chlorine water, the effect of hydrogen peroxide being less marked. The results indicate that the reduction-capacity is a measure of the antiscorbutic properties, and that the reducing substance is the carrier of vitamin *C*. J. G.

Toxicological and Forensic

Toxicity of Thiophen. F. Flury and F. Zernik. (*Chem. Ztg.*, 1932, **56**, 149.)—According to Rambousek's experiments (*Gewerbliche Vergiftungen*, 1911, p. 259), the vapour of thiophen is somewhat less poisonous than that of benzene. Experiments made by the authors, in conjunction with Thieme, show that the action of the vapour of pure thiophen is qualitatively similar to that of pure benzene vapour, but is distinctly the more poisonous. With mice, breathing of air containing 0·01 grm. of thiophen per litre produced collapse after 0·75 to 2·5 hours, and, in some cases, subsequent death, which was never caused by benzene in the same concentration. With 0·03 grm. of thiophen vapour per litre of air, death always occurred within 20 to 80 minutes, whereas a corresponding proportion of benzene vapour rarely proved fatal. It is possible that the toxicity of benzene may sometimes be greatly increased by the presence, as impurities, of unsaturated sulphur compounds. Thus, treatment of benzene containing ethylene with carbon disulphide may give rise to dichlorodiethyl sulphide ("mustard gas"). (*Cf.* Ditmar, *Chem. Ztg.*, 1931, **55**, 770.) T. H. P.

Group-specific Substances in Forensic Medicine. R. B. Lloyd. (*Brit. Med. J.*, 1932, 284–285.)—There are four blood groups dependent upon isoagglution reactions, the constitution and inheritance of which is best explained by Bernstein's hypothesis of three multiple allelomorphic factors A, B, and O.

Moss Group I = A + B
II = A + B or A + O
III = B + B or B + O
IV = O + O

The blood groups which contain the A factor are distinguished by the presence in the tissues and body fluids of Forssman's antigen. The serum of rabbits injected with this antigen becomes lytic for sheep red cells, owing to Forssman's heterophile antibody. Such a serum is prepared by injecting rabbits with washed Group II corpuscles. This anti-A serum is decomplemented, and by absorption with Group IV corpuscles anti-human precipitin is removed. This serum, still containing Forssman antibody, has been used by Schiff* to determine whether or not human material is derived from the A-containing groups. The test is carried out shortly as follows:—*Stage* 1—Incubate the extract or fluid, etc., with the test serum; *Stage* 2—Add sheep cells and complement. *Result*—If the extract contains the "A substance," there will be no haemolysis and *vice-versa*.

The test should prove useful, as it enables one to examine material other than blood, *e.g.* semen, saliva, and the organs of a cadaver. Further, the antigenic substance is a very stable body, and is often active in high dilution. But the widespread occurrence of animal species which contain Forssman's antigen limits the applicability of the test in medico-legal work to material the origin of which is unquestionably human, and uncontaminated in any way by such animal matter. Finally, it is not possible to immunise any animal against the B or O substances, which again limits the usefulness of the test. D. M. P.

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* *Über die gruppenspezifischen Substanzen des menschlichen Korpers.* By F. Schiff. (1931.) Gustav Fischer, Jena.

Bacteriological

New Autotrophic Bacterium which Oxidises Ammonia directly to Nitrate and Decomposes Petroleum. C. B. Lipman and L. Greenberg. (*Nature*, 1932, **129**, 204–205.)—A coccus or cocco-bacillus isolated from petroleum from a well over 8700 ft. deep, variable in size and somewhat so in shape, was found to grow well under strictly autotrophic conditions in an inorganic salt medium with ammonium sulphate or potassium nitrate as the source of nitrogen. It was found to oxidise the ammonia directly to nitrate, and this power was apparent much more quickly than with the nitrifying bacteria. It was also able to decompose petroleum without apparent gas formation, except for the end-product carbon dioxide, and it is apparently a facultative aerobe. D. G. H.

Chemistry of White Rots of Wood. II. W. G. Campbell. (*Biochem. J.* 1931, **25**, 2023–2027).—In a previous communication Campbell (*Biochem J.*, 1930, **24**, 1235) pointed out that comparatively little experimental work has been done on the chemistry of the particular type of wood decay in which lignin is decomposed, and, further, that it is unknown whether such decomposition is invariably accompanied by simultaneous decomposition of the wood carbohydrates. He showed that in the decay of wood by *Polystictus versicolor* (Linn.) Fr. carbohydrates are depleted as well as lignin. Falck (*Ber.*, 1927, **60**, 225) has concluded that in wood decayed by *Fomes annosus* cellulose is decomposed in the advanced stages. The study of the so-called white rots has now been continued by examination of the respective effects of *Armillaria mellea* (Vahl.) Fr. on beech wood, *Polyporus hispidus* (Bull.) Fr. on ash heartwood, and *Stereum hirsutum* Fr. on oak sapwood. It is concluded that the three samples of white rots examined have only one feature in common, and that this is shared by the white rot caused by *Polystictus versicolor.* In no case is there marked increase in the total alkali-solubility of the major components of wood substance, and, in the case of *Polystictus versicolor* and *A. mellea,* this is due to the fact that one component—namely, the pentosans not in the cellulose—becomes less soluble in 1 per cent. sodium hydroxide solution as decay proceeds. The white rots in question are thus sharply differentiated from the brown rots, for, in some of the latter, even in very advanced stages of decay, the residual wood substance is much more soluble in alkali than the original sound wood. Whilst it has been established that the detailed chemical effect on wood substance of both *Polyporus hispidus* and *Stereum hirsutum* is essentially similar in all respects, this effect can in turn be differentiated from that of *Polystictus versicolor* when the manner in which pentosans are decomposed is considered. *Polystictus versicolor* attacks the pentosans not in the cellulose to a greater extent than the pentosans which are associated with the cellulose, whereas *Polyporus hispidus* and *Stereum hirsutum* attack the pentosans in the cellulose, and have little or no effect on the pentosans not in the cellulose, at the stages of decay which were examined. In view of the effect on the alkali-solubility of wood substance of the decay caused by *Armillaria mellea,* and the fact that the decayed wood possesses to some extent the visual characteristics of a white rot, it must be concluded that in this type of rot a stage can exist in which lignin is apparently unaffected by the fungus; at the stage examined, decay by *Armillaria mellea* possesses chemical characteristics of both brown and white rots, but it may, with reason, be described as a variety of white rot. It has long been considered by biologists that in certain white rots of wood, where patches or pockets of a white material are found to occur, the fungi concerned have a selective action on lignin, and that the white residue consists entirely of cellulose. In the case of the "pocket" rot caused by *Stereum hirsutum*, it is concluded that this fungus cannot be credited with a selective action on lignin. The white patches were found to represent localities in a decaying mass in which decomposition has progressed to a greater extent than in the surrounding material. In these localities cellulose is decomposed as well as lignin, and, even after the development of the white colour, some lignin remains.

P. H. P.

Organic Analysis

Sensitive Means of Detecting Reducing Carbohydrates. P. K. Bose. (*Z. anal. Chem.*, 1932, 87, 110–114.)—When 2 c.c. of 25 per cent. sodium carbonate solution are treated with one drop of a 1 per cent. solution of *o*-dinitrobenzene in alcohol and a small quantity of an aqueous solution of a reducing sugar, and the mixture is heated for not quite one minute over a small flame, a deep violet coloration is produced. The smallest amount of sugar thus detectable in 1 c.c. of solution is 0·000006 grm. of dextrose, laevulose, galactose, mannose, rhamnose (hydrate), or lactose, 0·000003 grm. of arabinose, and 0·00001 grm. of maltose. In all cases, the colour appeared after the heating had lasted for 15 or 20 seconds, but it vanished if the heating was continued or if the liquid was left for longer than one minute. The test gave positive results with the ordinary reducing sugars and with glyceraldehyde, 4-β-glucosido-α-mannose, 4-β-galactosido-α-mannose, α-galacturonic acid, and penta-acetyl-β-glucose. Negative results were obtained with the ordinary non-reducing sugars and polysaccharides, glycerol, sorbitol, mannitol, dulcitol, α-methylglucoside, α-methylgalactoside, α-methylmannoside (α-methylmannopyranoside), 2:3:4:6-tetramethylglucose, 3:4:6-trimethylmannonic lactone, salicin, amygdalin, and lactic acid.

Hence, the reaction is shown only in presence of the grouping,

$$-CH(OH)\cdot CH(OH)\cdot O-,$$

and is negative with compounds containing the group

$$-CH(OH)\cdot CH(OR)\cdot O-,\ -CH(OH)\cdot CH_2\cdot OH,\ -CH(OH)\cdot CO_2H,\ \text{or}\ -CH(OCH_3)\cdot CH(OH)\cdot O-.$$

Penta-acetyl-β-glucose appears to be an exception, but the positive reaction obtained is probably due to liberation of glucose under the hydrolysing action of the alkali. The only aldehyde, either aliphatic or aromatic, which gives the reaction is formaldehyde in relatively high concentration; 5 drops of 0·58 per cent. formaldehyde solution fail to give the coloration under the conditions given above.

T. H. P.

Colour Reaction of Japanese Acid Clay upon Carotene in Palm Oil. K. Kobayashi, K. Yamamoto and J. Abe. (*J. Soc. Chem. Ind. Japan*, 1932, 35, 35B.)—The palm oil used was obtained from the Eastern Archipelago, and had the following constants:—Sp. gr. at 30° C., 0·9110; n_D^{30}, 1·477; acid value, 50·3; saponification value, 213·3; iodine value, 50·3. Japanese acid clay gives the deep bluish-green colour much more intensely than ordinary clays, kaolin, silica gels, etc. The best media to use are benzene, petroleum spirit, carbon disulphide, carbon tetrachloride, or chloroform. Ether, methyl or ethyl alcohols and acetone give no coloration. Colour reactions similar to the above are obtained with sulphuric acid, anhydrous zinc chloride, anhydrous aluminium chloride, phosphorus pentoxide, anhydrous ferric chloride, and anhydrous antimony chloride. It is considered that, in the case of Japanese acid clay, the colour is caused by polymerisation, rather than by condensation or dehydration. A study has been made of the absorption bands shown by the pigment extracted from palm oil by alcohol and by carotene from carrot, and, from the results, the authors conclude that the carotenes from these two sources are the same. R. F. I.

Horse Fat. J. Pritzker and R. Jungkunz. (*Z. Unters. Lebensm.*, 1932, **63**, 30–37.) The following data were obtained from fats prepared by the authors from 4 horses (10 to 21 years old):—Sp. gr. (15° C.), 0·9125 to 0·9198; refractometer reading, 51·5 to 53·1; acid value, 0·4 to 1·5; ester value, 194·2 to 196·0; saponification value, 195·6 to 196·7; iodine (Hanus), 74·4 to 78·5; Reichert–Meissl value, 0·33; Polenske value, 0·8; unsaponifiable matter, 0·31 to 0·50 per cent. (yellow-green in colour); cholesterol, 0·1 per cent. (m.pt. of twice-crystallised acetate, 111° C.); solid fatty acids, 24·3 to 27·0 per cent.; *iso*-oleic acid (*cf.* Grossfeld and Simmer, ANALYST, 1930, **55**, 451), 0·17 to 0·23 per cent.; arachidic acid, nil; Kreis rancidity reaction, negative; Bellier's reaction, red to orange-yellow; nitric acid reaction (fat layer), dark-brown. The colours of the fats were yellowish-brown, the consistence at 20° C. was oily, and the odour and taste similar to those of rape-seed oil. The fatty acids had refractometer reading, 38·6 to 40·3; neutralisation value, 203·8 to 206·2; mean molecular weight, 272·1 to 275·2; m.pt., 34·5° to 38·8° C. These results are compared with those of previous workers, and it is concluded that the maximum value of 69 for the refractometer reading, frequently given in the literature arises from a misprint for 59 in the early sources from which the data were taken (*cf.* König, *Chem. der menschlichen Nahr. und Genussm.*, 1910, **3**, 420). Fractional precipitation of the lead salts of the fatty acids (Kreis and Roth, *Z. Unters. Lebensm.*, 1913, **25**, 81) enables horse fat to be distinguished from lard, but will not detect 20 per cent. of the former in the latter. J. G.

A Hydrocarbon in Ishinagi Liver Oil. M. Tsujimoto. (*Bull. Chem. Soc. Japan*, 1931, **6**, 237–239.)—A hydrocarbon obtained from the liver oil of ishinagi (*Stereolepsis ischinagi*, Hilgendorf) has been subjected to a preliminary examination. The liver oil had the following characteristics:—Sp. gr. 15°/4° C., 0·9358; $n_D^{20°}$, 1·5070; saponification value, 146·2; iodine value (Hanus), 155·5; acid value, 11·8; unsaponifiable matter, 22·36 per cent. The unsaponifiable matter was treated with methanol, the precipitate deposited from the solution on standing was repeatedly washed, and a yellow-orange viscous liquid was obtained, retaining its colour after treatment of its ethereal solution with animal charcoal. The still impure substance had a high specific gravity (0·942 at 17°/4° C.) and $n_D^{17°}$, 1·54;

it was highly unsaturated (iodine value, 290·8), and formed bromine and hydrogen chloride addition compounds, the former containing 67·07 per cent. of bromine and the latter 30·85 per cent. of chlorine. D. G. H.

Unsaponifiable Matter of Calamary Oil. M. Tsujimoto. (*Bull. Chem. Soc. Japan*, **1931**, **6**, 289–293.)—The calamary oil obtained from the liver of *Ommastrephes Sloani pacificus* (Steentrap) (*J. Soc. Chem. Ind. Japan*, **1927**, **38**, 865) had the following characteristics:—Sp. gr. 15°/4°, 0·9298; $n_D^{20°}$, 1·4828; saponification value, 175·8; iodine value, 184·1; acid value, 20·5; unsaponifiable matter, 4·5 per cent. The methanol solution of the unsaponifiable matter was cooled, separated from the crystals, the mother liquid was concentrated, and, eventually, two solid and one liquid parts were obtained, which were examined in detail. The presence of cetyl, batyl, and selachyl alcohols was confirmed, oleyl and chimyl alcohols were probably present, together with a small amount of more highly unsaturated alcohols, and 48 per cent. of cholesterol was found. D. G. H.

Dibasic Acids in Sumach Berry Waxes [Japan Wax]. M. Tsujimoto. (*Bull. Chem. Soc. Japan*, **1931**, **6**, 337–341.)—The waxes, or, more correctly, fats, of the berries of four species of Japanese sumach trees have been examined, and were found to have the following characteristics:

Fat.	*Rhus vernicifera* DC.	*Rhus sylvestris* S. et Z.	*Rhus trichocarpa* Miq.	*Rhus toxicodendron* L.
Colour:	Brownish yellow.	Brownish black.	Dark brown.	Brownish black.
Sp. gr. at 100°/4° C.	0·8653	0·8679	0·8639	0·8895
M.pt.	52·5–53° C.	51–52° C.	49–50° C.	38–39° C.
Acid value	3·1	6·2	14·1	—
Saponif. value	209·5	202·9	205·2	208(?)
Iodine value (Wijs)	12·9	24·9	16·8	82(?)
Unsaponif. matter, per cent.	0·62	—	0·78	—
Fatty Acids.				
M.pt.	62° C.	56–57° C.	54–55° C.	ca. 51–52° C.
Neutralisation value ..	212·9	214·1	212·6	212(?)
Iodine value (Wijs)	12·8	14·6	17·1	26
Petroleum spirit insoluble substance (crude dibasic acids), per cent.	6·3	1·6	1·9	6·3

The fatty acids were treated by the lead salt precipitation method, and the crude dibasic acids were recrystallised. In urushi wax (*R. vernicifera*) these amounted to 6·3 per cent. of the fatty acids, and appeared to consist chiefly of eicosane dicarboxylic acid, $C_{22}H_{42}O_4$. In Yama-hazé wax (*R. sylvestris*) the dibasic acids amounted to 1·6 per cent., and in tsuta-urushi wax (*R. toxicodendron*) to 6·3 per cent., consisting mainly of heneicosane dicarboxylic acid, $C_{23}H_{44}O_4$. In the case of the Yama-urushi (*R. trichocarpa*) wax the nature of the substance isolated (m.pt. 102° C.) was not determined. D. G. H.

Dibasic Acids in Japan Wax. M. Tsujimoto. (*Bull. Chem. Soc. Japan*, **1931**, **6**, 325–337.)—Japan wax is obtained in Japan only from the mesocarp of

the berries of *Rhus succedanea*, L. (Haze-noki), which grows chiefly in the southwest of the country. The waxes used in the investigation had iodine values ranging from about 17·5 to 20·2, owing to a certain admixture of kernel oil, and it should be noted that, during bleaching, changes in composition occur and figures recorded outside Japan usually refer to such compounds, and are not comparable with those of the genuine wax. The percentage of dibasic acids (dissolving with difficulty in petroleum spirit) in the fatty acids varied from 5·2 to 6·1 per cent. The acids can be separated by fractional precipitation with a calculated quantity of lead acetate in alcoholic solution, or by distillation of the esters, and an investigation of their composition showed the main constituent to be heneicosane dicarboxylic acid, $C_{23}H_{44}O_4$, although the acid $C_{22}H_{42}O_4$ (eicosane dicarboxylic acid) also appeared to be present in fair proportion. The dibasic acids have the property of imparting a fineness of structure and opaqueness, involving coherency and tenacity, to the fatty acids, while the characteristic property of Japan wax—that it can be kneaded without adhering to the fingers—is due to the presence of glycerides of the dibasic acids. The term "japanic acid" of Geitel and van der Want (*Z. prakt. Chem.*, 1900, **61**, 151) is to be avoided, since this is not the only dibasic acid in Japan wax.
D. G. H.

Determination of *o*-Cresol. F. M. Potter and H. B. Williams. (*J. Soc. Chem. Ind.*, 1932, **51**, 59–60T.)—The method depends on the relation between the m.pt. and composition of mixtures of cresylic acid and cineole, and is, therefore, the reverse of that proposed by Cocking for the determination of cineole in eucalyptus oils (ANALYST, 1920, **45**, 370). A standard curve was drawn from the following data, which were obtained from mixtures of pure *o*-cresol (cryst. pt. 30·95° C.) and cineole (cryst. pt. 1° C.; b.pt., 175·5 to 177·4° C.):—One hundred per cent. of *o*-cresol, cryst. pt. of *o*-cresol-cineole complex 55·7° C.; 95, 54·2; 89·85, 52·5; 80, 49·2; 63·5, 42·8; 50, 36·3; 40, 30·3; 12·5 per cent., approx. 5° C. The apparatus consisted of a test-tube (0·75 inch diameter) containing the mixture, surrounded by a larger tube (1 inch diameter), which served as an air-jacket, and was itself immersed in a 400 c.c. beaker (2·5 inch in diameter), containing water at 5° to 10° C. below the cryst. pt. (determined from a preliminary trial). A quantity of sample (*e.g.* 2·80 grms. of cresylic acid) was mixed with cineole (*e.g.* 4·00 grms.), in such a proportion as to obtain the molecular ratio required by the cresol-cineole compound, and the mixture was then heated to about 15° C. above the crystallisation point, and the temperature read to 0·1° C. every 30 seconds during cooling, the mixture being stirred gently for 5 seconds before each reading. The true crystallisation point, independent of supercooling, was obtained by the method of Bell and Herty (*J. Ind. Eng. Chem.*, 1919, **11**, 1124), *i.e.* the readings were taken at noted intervals for 5 minutes after the temperature-rise due to crystallisation, and the portion of the temperature-time curve obtained after this rise was extended backwards until it intersected the portion of the curve preceding the rise at a point which corresponds with the true crystallisation point. A rise in temperature of 1° C. should be regarded as the maximum permissible, and supercooling, which is most pronounced when the *o*-cresol content islow, should be avoided by preliminary rapid cooling, or by seeding. Water should be avoided or removed by distillation, since (*e.g.*) 10 per cent. depresses the crystallisation point by nearly 10° C. Trial experiments on mixtures of pure *o*-cresol with the isomeric cresols, phenol, xylenols, neutral oils or guaiacol, gave results within 0·5 per cent. of the true value; since the optimum accuracy is obtained when over 30 per cent. of cresol is present, known weights of the pure substance should be added to the sample, if necessary, to give at least this quantity. J. G.

Inorganic Analysis

Analysis of Red Lead and Lead Dioxide. N. Busvold. (*Chem. Ztg.* 1931, **56**, 106–107.)—As an equally accurate alternative to the iodimetric method, which, owing to the consumption of iodide, is considered too costly for routine works' purposes, the following volumetric method is proposed for the evaluation of red lead and lead peroxide. It depends on the reduction of lead dioxide by hydrogen peroxide. A 5-grm. sample, contained in a tall 250 c.c. beaker, is mixed with 20 c.c. of nitric acid (sp. gr. 1·2) by means of a glass rod, and 50 c.c. of water are added. The suspension is titrated, very slowly and with constant stirring, with dilute hydrogen peroxide solution (10 c.c. of 30 per cent. hydrogen peroxide diluted to 250 c.c., standardised with permanganate) until practically all of the solid material has dissolved, and a brown turbid solution is obtained; the liquid is then heated on a water-bath until the solution becomes clear. (In the test experiments about 1 mgrm. of insoluble residue remained, which was neglected, since it did not contain lead peroxide). The small excess of hydrogen peroxide remaining in the solution is back-titrated with permanganate. The amount of lead peroxide is calculated from the equation $PbO_2+H_2O_2=H_2O+O_2+PbO$. Good agreement between the results given by this method and the usual iodide method was obtained. In the course of the preliminary work the author tested Lux's method, in which red lead is dissolved in dilute nitric acid with an excess of standard oxalic acid, the dissolved lead is precipitated by sulphuric acid, and the excess of oxalic acid remaining unoxidised is determined by titration with permanganate. This method was found to yield inaccurate results, owing to occlusion of oxalic acid in the lead sulphate precipitate. S. G. C.

Chemical Corrosion of Lead in Presence of Phenol. E. Da Fano. (*Giorn. Chim. Ind. Appl.*, 1932, **14**, 18–21.)—Not every tar is suitable for coating underground telephone cables as a means of protecting the leaden sheath of the cable from the corrosive action of the soil. The tar used must answer certain requirements. If it contains too much oil, this is partly carried away by the soil-water, which is enabled to penetrate to the lead and exert its corrosive effect. On the other hand, an excessive proportion of dry pitch in the tar may lead to cracking of the coating at the low temperatures encountered during transport, laying, or use. It seems, moreover, that phenol may accelerate the corrosion of lead, as it takes part in a cyclic process in which it is constantly regenerated. Hence, phenol should be present in the tar only in the smallest amount possible, although, since it corrodes lead only when water and carbon dioxide are also present, it is harmless as long as the tar coating remains continuous and impervious to water. The best service in this direction is given by specially-prepared tar having a dropping point (Ubbelohde) between 35° and 42° C. T. H. P.

Analysis of Silver Plating Solutions. R. M. Wick. (*Bur. of Standards J. Research*, 1931, 7, 913–933.)—Tests have been made of feasible methods for the determination of the constituents and impurities present in alkaline cyanide silver-plating solutions, and recommended methods are given for determining free cyanide, total cyanide, total effective cyanide, silver, carbonate, chloride, iron, copper, mercury, and ammonia. *Free cyanide* (*i.e.* the excess of alkali cyanide above the amount required to form complex cyanides of the metals present in solution):—To 20 c.c. of the plating solution is added 0·1 to 0·2 grm. of potassium iodide, the liquid is diluted to 250 c.c. and titrated with 0·1 *N* silver nitrate solution. The end-point is the first appearance of opalescence, and is best observed against a black background; 1 c.c. 0·1 *N* $AgNO_3 \equiv 0{\cdot}00980$ grm. NaCN or 0·01302 grm. KCN. *Total cyanide.*—Ten c.c. of the solution are diluted to 250 c.c. in a 500 c.c. flask of a distillation apparatus; 10 c.c. of dilute sulphuric acid (1 : 1) are added by means of a dropping funnel. The liquid is distilled down to half its original volume, the distillate being received in a flask containing 100 c.c. of sodium hydroxide solution (2 per cent.). The total cyanide, now present in the distillate as sodium cyanide, is determined by the silver nitrate titration described above. *Total effective cyanide* (*i.e.* the total cyanide, exclusive of ferrocyanide).—Fifty c.c. of the solution are diluted to 500 c.c.; to an aliquot part of this (25 c.c.), 50 c.c. of an ammoniacal sodium chloride solution (water containing 10 per cent. of sodium chloride and 0·2 per cent. of concentrated ammonia) are added, the liquid is titrated with 0·1 *N* iodine solution to the first visible turbidity, diluted to one litre, 5 c.c. of starch indicator (0·5 per cent.) added, and the titration continued until a permanent blue colour forms; 1 c.c. 0·1 *N* $I_2 \equiv 0{\cdot}00245$ grm. NaCN or 0·00326 grm. KCN. *Silver.*—The silver is determined by the Volhard thiocyanate titration method after evaporation "to fumes" with sulphuric acid to remove cyanide. If the presence of mercury is suspected the silver should be separated as silver chloride. *Carbonate.*—To the solution remaining after the determination of *free cyanide*, phenolphthalein indicator is added, and the liquid is titrated with 0·5 *N* hydrochloric acid until the pink colour is completely discharged; 1 c.c. of 0·5 *N* HCl ≡ 0·0530 grm. of Na_2CO_3 or 0·0691 grm. of K_2CO_3. *Chloride.*—Ten c.c. of the solution are heated with 20 c.c. of concentrated nitric acid (if the solution contains a high proportion of chloride, an excess of silver nitrate should be added) until the precipitate which forms becomes nearly white, and then for a further period of half-an-hour, the volume being kept constant by the addition of nitric acid; the liquid is diluted to 75 c.c., rendered alkaline with ammonia, and any precipitate of ferric hydroxide is filtered off, dissolved in nitric acid, and reprecipitated. The chloride in the combined filtrates is precipitated in the usual manner as silver chloride, which is weighed. *Ammonia.*—Fifty c.c. of the solution are titrated with 0·5 *N* silver nitrate solutions as described above for the determination of free cyanide. The liquid is diluted to 250 c.c., 10 c.c. of sodium hydroxide solution (10 per cent.) are added, and the ammonia is distilled and titrated as in the ordinary Kjeldahl method. *Iron, Copper, Mercury.*—Normal methods are employed, the cyanide being first expelled by heating with sulphuric acid.

S. G. C.

Determination of Beryllium in Alloy Steels. H. Eckstein. (*Z. anal. Chem.*, 1932, 87, 268–273.)—The following simple technical method for aluminium-free steel is based on the solubility of beryllium hydroxide in alkali. The borings (0·5 grm.) are dissolved in warm, strong hydrochloric acid, the solution oxidised with nitric acid (3 c.c.), and evaporated for the precipitation of tungstic acid and silica. The chloride filtrate is evaporated with 15 c.c. of sulphuric acid (1:1) till heavy fumes are evolved; after addition of a little water, the evaporation is repeated, and the mass taken up in 250 c.c. of water. The hot solution is treated with a little silver nitrate and ammonium persulphate, boiled for 10 minutes, and made faintly ammoniacal. The precipitate is collected, washed, dissolved in a little sulphuric acid and 5 c.c. of saturated ammonium persulphate solution, and the precipitation repeated. The precipitate is dissolved in dilute hydrochloric acid, and the solution poured into 200 c.c. of 20 per cent. carbonate-free caustic potash solution, which is vigorously stirred during addition and for 2 minutes afterwards. After an hour's standing, the precipitate is filtered off and washed, and the filtrate carefully acidified with hydrochloric acid (1:1), treated with a few drops of sulphurous acid and a slight excess of ammonia, and left overnight. Mechanical agitation for half-an-hour is stated to bring about quantitative precipitation of the hydroxide. The precipitate is collected, washed with water containing a few drops of ammonia, and ignited to constant weight over a blast burner. As it always contains a little iron, it is dissolved in hydrochloric acid, the iron determined volumetrically, and the calculated amount of Fe_2O_3 subtracted.

Ferroberyllium.—The solution of the metal in *aqua regia* is evaporated to dryness, the silica made insoluble by two evaporations with hydrochloric acid, and filtered off. An aliquot part of the filtrate (equivalent to 0·2 grm.) is precipitated with ammonia, and the precipitate ignited to constant weight as before. It is dissolved in hydrochloric acid, the iron determined volumetrically (method not stated), and the ferric oxide thus found is deducted. W. R. S.

Determination of Beryllium. L. Fresenius and M. Frommes. (*Z. anal. Chem.*, 1932, 87, 273–285.)—A painstaking critical investigation of the published processes, with test determinations of beryllium in complex alloy steels. The authors conclude that the five processes tested give concordant results provided all sources of error are eliminated, as in the following directions:

The drillings (5 grms.) are treated with 100 c.c. of strong hydrochloric acid and enough nitric acid to oxidise tungsten; the solution is diluted, boiled, and filtered. The filtrate is evaporated to a syrup and extracted with ether in the usual manner; the extracted aqueous solution is evaporated with sulphuric acid to the appearance of white fumes, the acid diluted, treated with a few grms. of solid persulphate and a little silver nitrate, and boiled until the chromium has been converted to chromate. The solution is precipitated with a faint excess of ammonia, the precipitate collected and washed with dilute ammonium nitrate solution, and dissolved in sulphuric acid. Persulphate treatment, precipitation, and filtration are repeated (precipitate = *A*).

(1) *Hydroxyquinoline Method* (ANALYST, 1928, 53, 508).—For steel containing aluminium. The precipitate *A* is dissolved in a small excess of hydrochloric

acid, the solution approximately neutralised with ammonia, treated with 0·2 grm. of oxalic acid, and warmed to 60° C.; the reagent (a 5 per cent. solution of the base in 2 *N* acetic acid) is added during stirring, followed by 2 *N* ammonium acetate solution (25 c.c. in excess of the volume required to form a permanent precipitate). The precipitate is collected in a porous crucible and washed with hot water until the washings are colourless. The beryllium in the filtrate is precipitated with a slight excess of ammonia. The precipitate is collected, washed with ammonium nitrate solution just alkaline to phenolphthalein, dried, ignited, and heated with hydrofluoric and sulphuric acids. The residual sulphate is decomposed by heating at 1100° C. and the beryllia ignited to constant weight.

Test for Impurities.—The oxide is heated with a little hydrofluoric and sulphuric acids; after some fuming the sulphuric acid is cooled, diluted with a little water, and heating to the fuming stage is repeated. The sulphate is dissolved in 100 c.c. of water; 20 c.c. are tested with molybdate mixture (P_2O_5: *a*), 20 with hydrogen peroxide (V_2O_5: *b*), 10 with persulphate and silver nitrate (Mn_3O_4: *c*); 40 c.c. are precipitated with hydroxyquinoline as before, and the precipitate ignited, weighed, and tested colorimetrically for vanadium if any appreciable quantity was found in *b*; the difference between the weight of the hydroxyquinoline precipitate and the V_2O_5 found by colorimetry, *plus* $(a+b+c)$, is subtracted from the weight of BeO found. (The correction amounted to 0·02 to 0·04 per cent., the steel assaying 0·96 per cent. of beryllium.)

(2) *Caustic Potash Method.*—For steel rich in manganese (*cf.* preceding abstract). The precipitate *A* is dissolved in a minimum of hydrochloric acid, and the solution poured very gradually into a platinum capsule containing 200 c.c. of warm, 20 per cent. caustic potash solution, as free as possible from carbonate. The liquid is boiled and filtered, the filtrate acidified with hydrochloric acid, concentrated, and made faintly ammoniacal; if the precipitate is yellow, it is re-dissolved and re-precipitated with addition of hydrogen peroxide. The liquid is then stirred for 5 minutes and left to clear. The precipitate is collected and washed with faintly ammoniacal ammonium nitrate solution, and the ammonia precipitation (with addition of peroxide if necessary) repeated. The precipitate is ignited to constant weight and tested for impurities as before.

(3) *Basic Acetate Method.*—The precipitate *A* is dissolved in hydrochloric acid; the solution is approximately neutralised with ammonia, diluted to 200 c.c., treated with a few drops of dilute acid and with ammonium acetate (quantity not stated), boiled, and stirred for some minutes. The precipitate is left to settle and filtered off, the filtrate concentrated to 100 c.c. and precipitated with ammonia. The precipitate is ignited, weighed, and tested for impurities (*supra*); phosphorus need not be considered, as it is precipitated with the basic acetate. The latter may be dissolved and re-precipitated, but it never yielded more than 0·01 per cent. Be.

(4) *Tannin Method* (ANALYST, 1928, **53**, 401). (For steel rich in vanadium).—The precipitate *A* is dissolved in dilute sulphuric acid, the solution neutralised with ammonia till faintly turbid, cleared with a drop of acid, treated with 30 grms. of ammonium acetate and 25 grms. of ammonium nitrate, and diluted to 500 c.c. After addition of 8 c.c. of glacial acid and a few drops of hydrogen peroxide the solution is

boiled and a strong excess of 10 per cent. tannin solution added all at once. The precipitate is collected and washed with dilute ammonium sulphate solution: the filtrate should be yellowish-brown, not mauve. The precipitate is dissolved in hot dilute sulphuric acid, the liquid nearly neutralised as before, and the precipitation repeated. The combined filtrates are evaporated with excess of strong nitric acid, and the residue gently heated for removal of ammonium salts, and then dissolved in water. If green, the solution is treated with ammonium acetate and hydrogen sulphide, and the nickel sulphide filtered off. The beryllium is precipitated, as before, with ammonia; the weighed beryllia is tested for impurities other than vanadium, which is precipitated by tannin.

(5) *Ammonium Sulphide Method.*—The precipitate *A* is dissolved in dilute hydrochloric acid, the solution treated with 20 c.c. of 20 per cent. tartaric acid solution, then with hydrogen sulphide, made ammoniacal, and ammonium sulphide is added. The filtrate from the sulphide precipitate is evaporated with excess of sodium carbonate and with potassium nitrate in a platinum dish; the residue is fused, and the melt taken up in water and acidified with hydrochloric acid. The solution is precipitated with ammonia, after addition of hydrogen peroxide if vanadium is present. The precipitation is repeated, the precipitate being ignited, weighed, and tested for impurities as before. W. R. S.

Use of Zinc Oxide in the Determination of Cobalt and Manganese. J. I. Hoffman. (*Bur. of Standards J. Research*, 1931, 7, 833–892.)—Tests have been made to determine the degree of completeness of the separations of cobalt and manganese from other metals by the zinc oxide method, particularly from the standpoint of steel analysis. The general method of precipitation adopted was to add to the weakly acid solution of the steel in hydrochloric or sulphuric acid (oxidised with nitric acid), contained in a 500 c.c. graduated flask, a suspension of finely divided zinc oxide (50 grms. of zinc oxide in 300 c.c. of water) in small portions at a time, with frequent shaking, until an excess was shown either by the initially brown precipitate becoming lighter in colour, or by a milky appearance in the liquid after allowing the precipitate to settle; the liquid was made up to the mark and an aliquot part of the liquid was filtered through a dry paper, the precipitate not being washed. The precipitate from a steel was found to contain all the iron, tungsten, vanadium, chromium, uranium, zirconium, titanium, aluminium, phosphorus, arsenic and tin; copper, molybdenum and silicon are not, however, completely precipitated. The separation of cobalt from iron is slightly incomplete if only a single precipitation with zinc oxide is made; the results obtained with steels containing from 3·65 to 9·66 per cent. of cobalt were low to the extent of 0·1 to 0·3 per cent.; for special work, therefore, the small quantity of cobalt co-precipitated with the iron should be recovered by dissolving the iron precipitate in hydrochloric acid and repeating the precipitation with zinc oxide. In the case of manganese the separation was found to be complete with one precipitation, no more than a few thousandths of one per cent. being co-precipitated with the iron, even with a steel containing 3·57 per cent. of manganese. The temperature (20° to 100° C.) at which the precipitation with zinc oxide was made had very little influence on the results. The separation of iron from nickel is not very satisfactory, owing to a tendency for nickel to be retained by the iron hydroxide precipitate, even after two precipitations with zinc oxide, *e.g.* with a high nickel steel (8·44 per cent.) there was a loss of 0·1 per cent. of nickel. Small amounts of sodium carbonate, which might be present as an impurity in the zinc oxide, are not objectionable if only a slight excess of the reagent is added. S. G. C.

Determination of Small Amounts of Sodium by the Magnesium Uranyl Acetate Method. E. R. Caley. (*J. Amer. Chem. Soc.*, 1932, **54**, 432–437.)—The lower limit in the amount of sodium which can be determined by the magnesium uranyl acetate method, as described in *J. Amer. Chem. Soc.*, 1929, **51**, 1664, *et seq.*, has been found to be 0·2 mgrm. Attempts have been made to adapt the method to smaller quantities of sodium by (*a*) using a more concentrated reagent, (*b*) using a more concentrated solution of the sample and less reagent. These modifications, whilst giving some improvement in permitting the determination of 0·1 mgrm. of sodium in pure sodium chloride solutions, were found to be, generally, of less use than the normal method, since other constituents of a sample, *e.g.* sulphates, ammonium salts, potassium salts, showed a greater tendency to interfere, and difficulties were experienced through constituents of the reagent itself crystallising out. S. G. C.

Preparation of Iodine-Free Bromine. G. M. Karns and H. C. Donaldson. (*J. Amer. Chem. Soc.*, 1932, **54**, 442–444.)—A method is described for the preparation of iodine-free bromine for use, *e.g.* in the micro-analytical determination of iodine. The impure bromine is washed by shaking, in a mechanical shaker, with water, into which the iodine passes as iodic acid; several successive quantities of water and long shaking are required to remove the last traces of iodine. The effectiveness of the method was tested by adding 0·1 per cent. of iodine to 453 grms. of bromine, and shaking this with six successive quantities of 500 c.c. of water for a total period of 44 hours. Analysis of the washings showed that the bulk of the iodine was removed in one washing for 4 hours; 100 grms. of the total of 246 grms. of purified bromine finally obtained were found to contain less than 1·5 thousandths of a grm. of iodine by a method in which the bromine was allowed to evaporate through a layer of water containing a small amount of sodium hypobromite; the aqueous liquid was treated with acidified sodium sulphite solution, evaporated to dryness after the addition of potassium carbonate, the residue extracted with alcohol, and the iodine finally determined volumetrically after conversion into iodic acid by bromine water prepared from the purified bromine.
S. G. C.

Microchemical

Micro-Determination of Carbon by the Wet Method. (Part I). H. Lieb and H. G. Krainick. (*Mikrochem.*, 1931, 9, 367–384.)—A micro-determination of carbon by wet oxidation is modified from the Nicloux–Boivin method (*Bull. Soc. chim. biol.*, 1927, **9**, 639–758; 1928, **10**, 1271; 1929, **11**, 1269). In the Nicloux–Boivin method about 16 mgrms. of substance were necessary, and the carbon determinations showed errors of 1 to 2 per cent. In the new method only 2 to 5 mgrms. of substance are used, containing 1 to 3 mgrms. of carbon, and the error is reduced to 0·1 to 0·3 per cent. The method is suitable for all organic compounds, and particularly biological material, which is often difficult to burn by the dry combustion process. The determination takes about an hour, but does not require continuous attention. The carbon is oxidised by heating it for 30 minutes at 130° to 140° C. with a mixture of silver dichromate and potassium dichromate in concentrated sulphuric acid. The silver dichromate accelerates the reaction, and renders the oxidation complete. The combustion gases are passed in a stream of oxygen through a tube containing a glowing platinum contact (as used in the Pregl halogen determination) behind which is a wad of silver wool to retain any halogens. The gases are then passed into the absorption chamber, containing $N/10$ baryta solution, through a bubbler of fritted glass (Schott, Jena, size of pore G.1), which makes the bubbles sufficiently small for complete absorption when the fritted glass is moistened with a drop of alcohol before use. The excess of baryta in the absorption chamber is then titrated in the cold with $N/20$ hydrochloric acid, with phenolphthalein as indicator. The titration is carried out in the absorption vessel without opening it, the tips of the burettes being fitted through holes in the stopper. In this way contact with the outer air is prevented, and the determination is carried out in a closed system. *Reagents.*—The oxidation mixture, which is purified so as to give no blank value, is prepared from 20 grms. of silver dichromate, 10 grms. of potassium dichromate and 200 c.c. of pure anhydrous sulphuric acid (sp. gr. 1·84). The mixture is heated at 120–130° C. for an hour in a stream of dry oxygen, passing through at the rate of 10 c.c. per minute, and is shaken at intervals. After cooling to 80° C., the mixture is transferred to a bottle with a narrow curved neck to prevent the entrance of dust. The solution contains 150 mgrms. of chromate salts per c.c. *Standard Solutions.*—(1) $N/20$ hydrochloric acid, containing 3 per cent. of barium chloride, dissolved in water (free from carbon dioxide) and standardised with sodium carbonate. (2) $N/10$ baryta solution, containing 1 per cent. of barium chloride, dissolved in thoroughly boiled water, and filtered if necessary. The standard solutions are kept in bottles attached to the micro-burettes, as used by Pregl in the micro-Kjeldahl method (Pregl, *Quantitative Organic Micro-analysis*, 2nd Ed., p. 115).

Oxidation is effected in a glass apparatus with a neck opening into a funnel, with a protecting cap. The chromic acid mixture is poured down the funnel, and the gas inlet tube, passing down the middle, has a ground-glass portion, which acts as the stopper of the oxidising vessel. With this device, on slightly lifting the gas inlet tube, the acid can be added gradually, and the sulphuric acid acts as an effective tap lubricant and prevents any leaks. The oxygen is used at a pressure of 5 to 5·5 cm. of mercury, and, if it contains organic impurities, it should be passed through a tube containing platinum asbestos heated to 600° C. The carbon dioxide and water are absorbed, as in the Pregl micro-combustion process in a bubble counter containing 50 per cent. potash, and a guard-tube containing ascarite and calcium chloride. The absorption apparatus is attached to a Marriotte flask to adjust the velocity and measure the volume of gases. Between the combustion tube and the absorption vessel is a long-handled glass stopcock.

Method.—The absorption vessel and inlet of fritted glass are carefully cleaned, and then 10 drops of neutral alcohol and two drops of 1 per cent. phenolphthalein are placed in the absorption vessel. The substance to be determined is weighed into a small open capillary tube with a solid handle, and is placed in the oxidising flask. The air is swept out of the apparatus with 40 c.c. of oxygen, at the rate of 6 c.c. per minute. The platinum contacts are heated, and the gas is turned off for a moment while 3 to 4 c.c. of the chromate oxidising mixture are added from the funnel. The oxygen is turned on again, and, while the long-handled stopcock is turned off, 8 c.c. of $N/10$ baryta are added to the absorption vessel from the micro-burette. The oxidation vessel is then immersed in the heating bath already at 70° to 80° C., the stopcock is adjusted to give a flow of 2 to 2·5 c.c. of gas per minute, and the temperature of the bath is raised to 130° to 135° C., and held constant. After about 10 minutes, when the first cloudiness is observed in the absorption vessel, 100 c.c. of oxygen are passed through the apparatus to drive out all the carbon dioxide. The last 50 c.c. may be passed through at the rate of 3 to 3·5 c.c. per minute. The titration is carried out in a stream of oxygen of 3·5 to 4·5 c.c. per minute to stir the liquid. One c.c. of $N/20$ baryta $\equiv$ 0·3 mgrm. of carbon. Fifteen different substances were tested, and excellent results were obtained.

J. W. B.

Micro-gravimetric Determinations with Minute Quantities of Material, using the Electro-magnetic Micro-balance. E. Wiesenberger. (*Mikrochem.*, 1932, **10**, 10–26.)—An electro-magnetic micro-balance of the Angstrōm type, as improved by Emich (Abderhalden, *Handbuch der biochem. Arbeitsmethoden*, Abt. 1, [iii], p. 259), is used for the determinations. This can be used for weighing amounts down to 0·015γ. Details of the construction of the balance are given, including the making of the quartz threads and hooks and the fixing of the suspension and pointer. The balance is enclosed in a five-sided beech-wood case, the fifth side of which is made of aluminium, and fixed with wood at a distance of 1·5 cm. from the wall of the room, so as to give an enclosed pocket of air. A small window in the third wall of the case is made of "Robon glass" (Schott, Jena), which absorbs heat rays, and through this the light from a lamp is directed on to a mirror which throws the rays into a telescope, through which the movements of the pointer are observed. During a weighing the magnetised pointer is restored to its original position by altering the current through an electro-magnet, and the weights are compared from the readings on a millivoltmeter. The null point of the balance remains very constant, though it is disturbed by thunderstorms.

The balance is used for the determinations of metals in salts by conversion into the sulphate, and for the electrical determination of copper. The weight used for each determination is 1 to 12γ or 50 to 100 times less than by the Pregl method. The substance is weighed out into a small platinum crucible (diameter of 3 mm.), made of foil, 0·003 mm. thick, with a hook handle of fine platinum wire; the weight is about 5 mgrms. For the determination of salts a small drop of sulphuric acid is placed on the substance by means of a glass thread as fine as hair, on the tip of which a minute drop has been placed with a hair-fine capillary. The micro-crucible is then placed in a porcelain crucible, suspended from a quartz hook and gently heated with the pilot flame of a Bunsen burner. After a few minutes the heating can be increased. Determinations on lead formate, potassium tartrate and sodium chloride were made, with maximum errors of less than 1 per cent. Electrometric determinations of copper were carried out, using the micro-crucible itself as the cathode on which the copper was deposited as follows:—The copper salt is weighed out and dissolved in 1000 times its quantity of dilute sulphuric acid, so that the liquid almost fills the crucible; this is suspended and supported by the wire which is connected with the source of current. The platinum anode is carefully dipped into the solution, the poles are connected with a single-cell lead electrode, and the solution is electrolysed for 30 minutes at a potential of 2 volts. The crucible is washed with alcohol, and then with water, while the current is still running; it is then disconnected, dipped first into water, and then into alcohol, dried at 120° C. for 5 to 10 minutes, and re-weighed. The results with 7 to 12 mgrms. of copper sulphate and copper rubidium sulphate differed from the theoretical amounts by 0·05 to 0·3 per cent. J. W. B.

Physical Methods, Apparatus, etc.

Compensator for Constant-Volume Gas Burettes. H. R. Ambler. (*J. Scientific Instruments*, 1931, 8, 374–376.)—The constant-volume gas analysis apparatus, described in ANALYST, 1929, **54**, 517, has been fitted with a compensator for variations in temperature and barometric pressure. The device is found to save time and increase accuracy, and is adaptable to other instruments, of both the constant-volume and constant-pressure types. S. G. C.

Portable Apparatus for Precise Gas Analysis. H. R. Ambler. (*J. Scientific Instruments*, 1931, 8, 369–373.)—A portable form of the apparatus described in ANALYST, 1929, **54**, 517, has been developed. The size of the apparatus, complete in case, is 15 by 12 by 4½ inches, the weight 8½ lbs., and the attainable accuracy 0·1 per cent. S. G. C.

Interpretation of Photomicrographs (of Leather Fibres). D. Jordan Lloyd and R. H. Marriott. (*J. Int. Soc. Leather Trades Chem.*, 1932, 16, 57.)—The fibre-bundles of skin are composed of fibres, and these consist of still finer elements, the fibrils. The fibre-bundles are interwoven in all directions, but, for purposes of classification, the types of weave can be defined as vertical, high angle, medium angle (about 45° to the grain surface), low angle and horizontal. Regularity of weave pattern is always found in first-class leathers. The fibre-bundles can be loosely or compactly woven together. A loose weave indicates a soft, and, except in the case of glove leathers, an undesirable leather. The fibres can be thick or thin, and by the thickness of the outline of the fibres, although some fibres may be naturally thin, such fibres can be differentiated from fibres in which the thinness is caused by errors in process, provided that the adjustment of the microscope is standardised and the refractive index of the mounting medium is constant. The thickness of the outline is also dependent on the closeness of the packing together of the fibres, but the causes of the variations in the thickness of the outline of fibres can easily be distinguished. The various liquors used in the tannery can affect the separation not only of the fibres, but also of the fibrils from one another. Where the fibres possess longitudinal striations, and the cross section of the fibre-bundles is full of fine markings, indicating the presence of the fibrils, the fibres are said to be "split." Where the "splitting" is so pronounced that the fibrils are separated from each other, and the fibre-bundle loses its definite outline, the fibre-structure is said to show "separation." In general, "splitting" is desirable if flexibility be desired, but "separation" generally indicates a soft, flabby, porous leather. Examples of all these types of structure are given by means of photomicrographs.

Reviews

EXAMINATION OF WATER, CHEMICAL AND BACTERIOLOGICAL. By WILLIAM P. MASON. Sixth Edition, revised by ARTHUR M. BUSWELL. Pp. xi+224. New York: John Wiley & Sons; London: Chapman & Hall. 1931. Price 18s.

Five editions of this work have appeared at intervals from the pen of Professor Mason; the first was apparently published in 1899, the fifth in 1917. The present edition has been revised by Professor Buswell alone. It is obvious that the book has met a demand, at least in the country of its origin. Its purpose, we are told, "has always been to supply the needs of the undergraduate student rather than those of the routine analyst." This edition appears in an entirely new format, with few alterations or excisions, but with extensive additions.

Chapters I and II (to p. 102) are chiefly concerned with the chemical, and Chapter V (pp. 146–162) with the bacteriological examination of water as to its suitability for drinking and general domestic purposes. These chapters contain practically all of the previous edition; additions include some account of the determination of the pH value, and information concerning the chemical substances found in natural water, and the waste of soap caused by hardness. In connection with the last matter, the erroneous statement is made that "one gallon per capita per day is usually taken as the amount of water used for washing." The analytical procedures detailed are substantially in accordance with the Standard Methods of the American Public Health Association (first published in 1905), which have been so generally adopted in America. They present no new features of importance. The low results obtained for nitrates in presence of high chlorides with the phenolsulphonic acid process (if the method given for the removal of chlorides is not utilised) would not be prevented by adding sodium chloride to the "standards," as the loss occurs during the reaction with the phenolsulphonic acid; no mention is made of the simple modification of the process which eliminates the error due to this cause. Nessler solution does not improve with age. The method given for examination for poisonous metals does not distinguish between lead and copper; it will occasion some surprise that it is considered that this is not commonly necessary. In the determination of free and albuminoid ammonia, Wanklyn, who devised the process (in 1867), returned the results in terms of NH_3, and this notation has been generally followed; in the Standard Methods, to which reference has been made, the ammonia results are returned in terms of N. By changing the strength of the standard ammonium chloride solution (in the fifth edition) the author brought his book into line with American practice, but, in doing so, failed to realise that the scores of analytical results of these determinations transcribed from the earlier to the present edition are misleading to the extent of the gross error represented by the difference between 3·82 and 3·15.

With regard to the interpretation of the results of an analysis, the author says: "The intention is simply to place before the reader sundry data and the opinions of various authorities, and absolutely disclaim any desire to set boundaries to the free use of the analyst's good judgment." It is, however, rather difficult to understand how the student just commencing a study of the subject is competent to exercise such judgment. The probability of correct conclusions being reached would have been increased if the author had devoted some of the space given to the opinions expressed in the literature of the '80's and '90's of last century to an extended exposition of the findings in his own experience.

Chapter III (pp. 103–135) deals with routine laboratory methods for the determination of mineral constituents. For the control of water-softening processes the Standard Methods of the American Railway Engineering Association are reprinted, and for examination of water as to suitability for boiler purposes, the methods of the Illinois State Water Survey (of which the present author is chief) are detailed. For the continually increasing pressure at which boilers are now being worked, phosphate is being employed in increasing quantity for treatment of feed water, and Straub's method (1930) for this determination is given; one of the two standards referred to appears to have been omitted in the description of the process. This section concludes with an account of the methods used by the Illinois State Water Survey in the examination of mineral (medicinal) waters.

Chapter IV (pp. 136–145) appears to be a direct reprint of class instruction sheets for laboratory exercises in clarifying, softening, and chlorinating of water; the strength of the chlorine solution specified works out as ten parts, and not one part per million, as stated. The information given is, presumably, intended to be supplemented by verbal instruction.

There is an extended appendix (pp. 163–217) which contains much of interest, but which could have been drastically condensed without disadvantage. The most important section is a reprint of the U.S. Treasury Department Standards for drinking and culinary water supplied by common carriers in interstate commerce, which, though this is not stated, have been extensively adopted for public supplies in general.

This edition, especially when compared with the preceding one published fourteen years previously, exhibits evidence of what is usually termed "hasty" revision. Examples of this are (with page numbers) repetition of definition of Continental degrees of hardness (24, 42); sulphonic instead of sulphanilic uncorrected (50); designation of "recent" retained (54, 87); purpose of ammonium hydroxide is explained (54), but potassium hydroxide is specified (56); repetition to decolorise (56, 57); Welsbach burner recommended if daylight not available (67); albuminoid ammonia changed to albuminoid nitrogen, but only in some cases; indiscriminate absence of 0 before the point in decimal figures less than unity; dichromate (95) reverts to bichromate (97). There are about a dozen typographical errors, none of them serious. ROBERT C. FREDERICK.

THE BIOCHEMISTRY OF MUSCLE. By DOROTHY MOYLE NEEDHAM, M.A., Ph.D., Biochemical Laboratory, Cambridge. Pp. viii+166. London: Methuen & Co., Ltd. 1932. Price 5s. net.

Methuen's Monographs on Biological Subjects, of which Dr. Needham's work is the fourth, aim "to give brief but authoritative accounts of the present state of knowledge in various departments of Biology." The biochemistry of muscle has just emerged from a serious but very interesting crisis, and a publication on this subject from the pen of an authority who has been actively engaged in research on these lines, is both opportune and welcome. Until 1898, when Fletcher commenced his far-reaching investigations on muscular energy, it was generally believed that this form of energy depended on a sudden production of an unstable compound, which contained oxygen ready for the production of energy by oxidation. These purely theoretical speculations have now been replaced by well-established facts, the logical sequence of which is well developed in the work under review. Dr. Needham traces the problem with precision, from lactic acid metabolism by spontaneous oxidation to the concept of a muscle-machine, and throughout weighs with care the different views and experimental data, often contradictory amongst themselves, which have been put forward to account for the phenomena of muscular energy. *The Biochemistry of Muscle* is a well-written and welcome addition to biochemical literature, and we are indebted to Dr. Needham for having collected and sifted this material.

In conclusion, one feels inclined to suggest that when the second edition is considered it would perhaps be advisable to omit the "Glossary" (pp. 153–155). It adds little to the value of the book, and perhaps lowers its standard. After all, who does not know that "aldose" is "a sugar containing the aldehyde (CHO) group"? M. NIERENSTEIN.

CLINICAL CHEMISTRY IN PRACTICAL MEDICINE. By C. P. STEWART, M.Sc. (Dunelm.), Ph.D. (Edin.), Lecturer in Biochemistry, University of Edinburgh; Senior Biochemist, Royal Infirmary, Edinburgh, and D. M. DUNLOP, B.A. (Oxon.), M.D., M.R.C.P. (Edin.), Assistant, Department of Therapeutics, University of Edinburgh. Pp. x+246+2 for Notes. Edinburgh: E. & S. Livingstone. Price 7s. 6d. net.

Laboratory workers are apt to be over-enthusiastic, and they tend to underestimate the value of bedside observations. To be reminded that biochemistry is not the philosopher's stone of medicine is a healthy warning to all concerned with the usual routine in a laboratory attached to an infirmary. Valuable as biochemical investigation is, it must always be considered in conjunction with clinical examination, a point clearly demonstrated by Drs. Stewart and Dunlop, whose book will be found not only of practical use, but also stimulating. There have been many works written on chemical routine in connection with medicine, but we know of no other book of its size where clinical experience has been so well tempered with laboratory routine. Few chemists have such opportunities as are to be found at the Royal Infirmary at Edinburgh.

It is beyond the limits of a review to discuss in detail and to evaluate the different methods, and the preferences for some of the processes described, as, for example, the collection and preservation of samples, the study of basal metabolism and of the mechanism of neutrality in the living organism, and the many other topics so vital to laboratory routine. Each of the twelve chapters is permeated with practical laboratory experience, and at the same time with clinical understanding. Obviously, only those who use the book are in the position to judge its practical application, but, meanwhile, one can say, with confidence, that it deserves the serious attention of those who require a manual for use in the clinical laboratory.

M. NIERENSTEIN.

REVIEW OF THE EFFECTS OF ALCOHOL ON MAN. Edited by K. KITCHIN and D. H. KITCHIN. Pp. 300. London: Victor Gollancz, Ltd. 1931. Price 8s. 6d.

An enquiry into the medical, social and economic aspects and dimensions of the alcohol problem in Great Britain was initiated by a group of persons of wide public interests, *viz.* Lord Buckmaster, Lord Balfour of Burleigh, Field-Marshal Lord Methuen, the Hon. Mrs. Alfred Lyttelton, the Right Hon. Philip (now Lord) Snowden, and Mr. W. D. Hitchens.

This enquiry was instituted before there was any sign of the appointment of the recent Royal Commission on the subject of alcohol.

Two Committees were appointed, one to deal with the social and economic side of the problem, the other with the medical. The present work is the Report of the Medical Committee.

The various aspects of the subject are dealt with in separate chapters by authors who have made a special study of the particular branch of the problem on which they write, and all are recognised authorities. It would have been difficult to have chosen a better team.

Dr. Kathleen Kitchin and Mr. D. Harcourt Kitchin have carefully edited the various contributions and, without altering their context, have, by elimination of unnecessary repetition, made a compact and harmonious whole of the isolated chapters.

Chapter I, by Dr. Howard Florey, gives an admirable summary of the physiological actions of alcohol which is worthy of very close study. The physiological action on the circulatory, respiratory, digestive and nervous systems are considered in detail, and the conclusion is arrived at that the action of alcohol on the highest parts of the central nervous system is narcotic and not stimulant.

This conclusion is in agreement with that of the other writers, who deal with the subject from different angles. It is shown that alcohol can be oxidised in the body for the production of useful work, when given in amounts producing physiological rather than pathological conditions.

Dr. G. Roche Lynch, in Chapter II, gives a very valuable review of the toxicology of alcohol. The recent work on the absorption and excretion of alcohol is summarised, and the various percentages of alcohol in the blood are compared with the corresponding clinical symptoms caused thereby.

The curves illustrating the rates of excretion of alcohol, when taken in the form of whisky or stout, are produced, and a most interesting series of drawings, made by the subject of this experiment, illustrates the effect of alcohol on the co-ordinating action of the nervous system.

Acute and chronic alcoholic poisoning are fully dealt with from the toxicological aspect, and also the influence of such factors as the kind of beverage, the relationship of the taking of food with alcohol, idiosyncrasy, tolerance, and special acquired susceptibility.

The addiction habit of alcohol is compared and contrasted with that of drug addiction (morphine).

Chapter III relates to the effect of alcohol on the body resistance to disease, and in it Professor F. S. Langmead and Dr. T. C. Hunt show that, while profound excess markedly reduces the body resistance, there is no evidence proving that in the physiological amounts taken by the temperate drinker any effect is produced on the essential processes of immunity and protection.

Dr. Bedford Pierce, who is so well qualified to deal with this aspect of the subject, gives in Chapter IV a most interesting summary of the mental effects of alcohol.

Chapter V, by Dr. Isabel G. Wilson, deals with alcohol and mental disorder in an admirably fair and well-balanced summary of this much-disputed question.

The morbid changes caused by alcohol are very carefully and critically reviewed in Chapter VI by Dr. W. D. Newcomb, whose great post-mortem experience entitles him to speak with authority. He points out that alcohol has been credited as being the aetiological factor in a number of diseases, such as arterio-sclerosis, nephritis, etc., where the scientific evidence fails to support the past conclusions. In some diseases, such as cirrhosis of the liver, while alcohol may often play an important causative part, it is clearly shown that other factors are also at work.

Professor F. S. Langmead and Dr. T. C. Hunt, in Chapter VII, give an admirable account of the use of alcohol in the practice of medicine. They point out that, while the use of alcohol as a therapeutic remedy is very much less common than in the past, yet the real deciding factor is the clinical effects produced by it in certain diseased conditions. They state that alcohol is a valuable drug, but there are limitations to its actions, and its prescription requires skill and discretion.

Chapter VIII, by Dr. F. A. Crew, gives a most interesting biological study of the racial effects of alcohol. The subject is dealt with in a most instructive and novel manner, and the influence of alcohol is impartially and clearly reviewed.

The Appendix deals with the various forms of alcohol other than ethyl alcohol, and gives a very useful table of the various alcoholic beverages, with their source, descriptive remarks, and respective alcoholic content.

This work gives the most concise and accurate review of the medical aspects of alcohol which has been yet published. It should be in the possession of every analytical chemist who is concerned with the analysis of alcoholic beverages. It is of the utmost value to medical men and chemists who are confronted with the medico-legal aspects of the effects of alcohol. It should be included in every medical and chemical library.

W. H. WILLCOX.

Publications Received

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Fifth Edition. Vol. IX. Edited by C. AINSWORTH MITCHELL. (*Proteins of Plants*, by D. Jordan Lloyd; *Proteins of Milk*, by G. D. Elsdon; *Milk*, by J. Golding; *Milk Products*, by E. R. Bolton; *Meat and Meat Products*, by C. R. Moulton.) London: J. & A. Churchill. Price 32s.

APPLIED PHARMACOLOGY. By A. J. CLARK. London: J. & A. Churchill. Price 17s.

STRUCTURE AND COMPOSITION OF FOODS. By A. L. WINTON and K. B. WINTON. London: Chapman & Hall. Price 53s. net.

MICROBES AND ULTRAMICROBES. By A. D. GARDNER. London: Methuen & Co. Price 3s. 6d.

MAKERS OF CHEMISTRY. By E. J. HOLMYARD. London: Oxford University Press. Price 7s. 6d. net.

WATER DIVINERS AND THEIR METHODS. By HENRI MAGER. Translated by A. H. BELL. London: Bell & Sons. Price 16s. net.

HYDROGEN IONS. By H. T. S. BRITTON. London: Chapman & Hall. Price 25s. net.

THE PRACTICE OF ABSORPTION SPECTROPHOTOMETRY. Published by Adam Hilger, Ltd. Price 5s. net.

RECENT APPLICATIONS OF ABSORPTION SPECTROPHOTOMETRY. Published by Adam Hilger, Ltd. Price 3s. 6d. net.

ANNUAL REPORTS ON THE PROGRESS OF APPLIED CHEMISTRY. Vol. XVI. Society of Chemical Industry. Price 7s. 6d. to Members; 12s. 6d. to non-Members.

ALCOHOLIC FERMENTATION. By A. HARDEN. London: Longmans, Green & Co., Ltd. Price 15s. net.

BRITISH CHEMICALS AND THEIR MANUFACTURERS. 1931. The Association of British Chemical Manufacturers. Supplied gratis to users of chemicals.

MAY, 1932 Vol. LVII., No. 674

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, April 6th, the President, Mr. F. W. F. Arnaud, being in the chair.

Certificates were read for the first time in favour of:—Reginald Haydn Hopkins, D.Sc., F.I.C., and William Basil Walker, B.Sc., A.I.C.

Certificates were read for the second time in favour of:—Edward Bertram Anderson, M.Sc., F.I.C., Edward Foster Eaton, Frank Maudsley, B.Sc., F.I.C., James William Thom, B.Sc., and Samuel Gordon Stevenson, B.Sc., B.Pharm., F.I.C.

The following were elected Members of the Society:—Alan Arthur Douglas Comrie, B.Sc., A.I.C., Edwin William Stanley Press, B.Sc., A.I.C., and Muriel Roberts, B.Sc., F.I.C.

The following papers were read and discussed:—"The Estimation of Hormones," by K. Culhane, B.Sc., A.I.C., and S. W. F. Underhill, M.A., B.M., B.Ch.; "The Chemical Assay of Thyroid Gland," by G. Middleton, B.Sc., A.I.C.; "The Water-Protein Ratio of Lean Meat, and its Bearing upon the Analysis of Sausages," by F. W. Jackson, B.Sc., A.I.C., and Osman Jones, F.I.C.; "Nitrite in Cured Meats," by Osman Jones, F.I.C.; and "Notes on the Freezing Point of Milk," by H. C. Lockwood, B.Sc., A.I.C.

NORTH OF ENGLAND SECTION

A Joint Meeting of the Section with the Liverpool and Manchester Sections of the Institute of Chemistry and other bodies was held in Manchester, on April 9th, 1932.

In the absence of the Chairman (Mr. J. Evans), Prof. W. H. Roberts presided over a large attendance. Dr. G. Roche Lynch gave a lecture on "Poisons and Poisoning," which was followed by a discussion.

Obituary

SIR WILLIAM SMITH

We regret to record the death, on March 17th, of Sir William Robert Smith, who had been a Member of the Society since 1892.

Sir William was born in 1850, and, after graduating in medicine at Aberdeen, became Medical Officer to the old London School Board. In 1886 he founded the British (now the Royal) Institute of Public Health, and for the rest of his life his work was closely associated with that of the Institute, of which, at the time of his death, he was still Principal. In addition to his work in connection with that Institute, he held the appointments of Public Analyst for the County of Berkshire, the Boroughs of Newbury and New Windsor, the Metropolitan Boroughs of Paddington and Woolwich, and the City of Oxford.

He was also Emeritus Professor of Forensic Medicine and Toxicology at King's College, London, and he edited the seventh edition of Guy and Ferrier's *Forensic Medicine.*

In 1918 he was knighted, after serving as Sheriff of the City of London.

The Council has sent, on behalf of the Society, a letter of sympathy to Lady Smith.

EDITOR.

Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates

XXII. The Separation of the Earth Acids from Metals of the Hydrogen Sulphide Group

By E. F. WATERHOUSE and W. R. SCHOELLER, Ph.D.

(Work done under the Analytical Investigation Scheme)

(*Read at the Meeting, November* 4, 1931)

The mineral associates of the earth acids in the hydrogen sulphide group are: (1) antimony (in stibiotantalite); (2) bismuth (in bismuthotantalite); (3) tin (subordinate amounts in most earth-acid minerals); (4) lead (less than one per cent.) accompanies uranium; and (5) copper (very small amounts in a few minerals). Arsenic, selenium, tellurium, silver, mercury, and cadmium cannot be described as mineral associates of the earth acids. Germanium may be present in traces, but its isolation calls for a special procedure and for substantial quantities of material.

In endeavouring to work out a separation process of practical value, we decided that, as the process would be preceded by the decomposition of the mineral, the test analyses should be made by the same procedure; since, by mixing separately-prepared solutions of known metal content, we should be disregarding the possibility of complex-formation during the lixiviation of the melt. Hence also, the completeness of the separation should be proved by the quantitative recovery of the earth acids as well as of the metals of the hydrogen sulphide group.

Now the decomposition procedure proposed by Schoeller and Powell (I, ANALYST, 1922, **47**, 93), and applied in the present investigation, is fusion with bisulphate, followed by lixiviation with tartaric acid. In this process, any lead present is converted into and eliminated as insoluble sulphate, together with silica and the bulk of the stannic oxide. The filtrate is saturated with hydrogen sulphide, and the precipitate examined for any member or members of the group. Of these, lead has already been removed as sulphate. The separation of tin from the earth acids has been discussed in Section XX (ANALYST, 1931, **56**, 795). There remain antimony, bismuth, and copper to be considered in this Section. In a process effecting a satisfactory separation of these metals as sulphides from the earth acids, it may, we submit, be taken for granted that any small quantities of tin (arsenic) present in the solution will accompany the antimony, and any traces of lead, silver, etc., the bismuth and copper.

A. ANTIMONY AND EARTH ACIDS.—Two time-honoured but ineffective procedures (Berzelius; Rose) for the separation of tin and antimony from the earth acids have been criticised in an earlier Section (VIII, ANALYST, 1927, **52**, 507, 509); hence further discussion of them is unnecessary.

Foote and Langley's Process.—A separation process which, no doubt, combines accuracy with simplicity, is given by Foote and Langley for the analysis of stibiotantalite (*Amer. J. Sci.*, 1910, **30**, 398). It consists in dissolving the powder (1 grm.) in 20 c.c. of hydrofluoric acid, diluting to 300 c.c., and passing a stream of hydrogen sulphide. The precipitate is treated with ammonium sulphide for the separation of a little bismuth from the antimony sulphide. The fluoride filtrate is evaporated with sulphuric acid, diluted, and the earth acids precipitated with ammonia.

We do not wish to criticise Foote and Langley's method, but submit that the process given below is more generally applicable, and does not involve the use of hydrofluoric acid.

Authors' Investigation.—Our first test analyses by Schoeller and Powell's method (*vide supra*) disclosed a variable, but appreciable, shortage in the earth-acid recovery. The mixed oxides were fused with bisulphate, the clear tartaric solution of the melt treated with hydrogen sulphide, and the antimony in the sulphide precipitate determined volumetrically by permanganate. The filtrate from the antimony sulphide was submitted to tartaric hydrolysis, followed by tannin precipitation (XIX, ANALYST, 1931, **56**, 306). By re-treating the sulphide precipitate we proved that it contained earth acid; in a few experiments the amount of earth acid occluded in the sulphide precipitate was determined separately, with the following results: 0·0057; 0·0036; 0·0046; and 0·0022 grm. In our experience, metallic sulphides precipitated from acid tartrate solution containing earth acid are invariably thus contaminated.

This may be explained by the following considerations: Tartaro-tantalic acid (and, in a lesser degree, tartaro-niobic acid) is a rather unstable complex, subject to hydrolytic dissociation in acid solution; thus, when a large excess of mineral acid is added to the boiling solution, the earth acid is almost quantitatively precipitated ("tartaric hydrolysis"). In cold, weakly acid solution, partial dissociation takes place gradually with formation of a colloidal phase, and the solution, even though quite clear at first, eventually deposits a flocculent precipitate. The flocculation of the earth acid is, no doubt, assisted by that of the sulphide precipitate, and accelerated by warming and by the coagulating effect of hydrogen sulphide. In the same way, contamination of hydrogen-sulphide precipitates with titania can be brought about in weakly acid sulphate solutions.

In the next series of tests we proceeded as follows: Solution of the sulphide precipitate in strong sulphuric acid; permanganate titration; re-precipitation of antimony sulphide, filtration; volatilisation of the antimony by heating the precipitate with bromine and hydrochloric acid; recovery of the co-precipitated earth acid from the residue combined with the sulphide filtrate. This rather elaborate procedure was abandoned as being applicable to antimony (tin), but not to the hydrogen sulphide group as a whole.

A quantitative separation was finally achieved by a re-treatment in ammoniacal solution, included in the following sequence of manipulations: Solution of the sulphide precipitate in sulphuric acid; addition of tartaric acid and excess of ammonia; treatment with ammonium polysulphide; acidification with acetic acid, boiling, and filtration. The re-precipitated sulphide was now free from earth acids, which were found in the filtrate.

The treatment just outlined not only separates antimony from the earth acids, but also forms the basis of the group separation procedure described below.

B. BISMUTH AND EARTH ACIDS.—So far as we know, the only reference to bismuth in the literature on the subject occurs in Meyer and Hauser's monograph, *Die Analyse der seltenen Erden und der Erdsäuren* (p. 271); the passage merely states that pyrosulphate hydrolysis (*cf.* XII, ANALYST, 1928, **53**, 467) affords a good separation of the earth acids and titania from most metallic elements, with the exception of tin, tungsten, silicon, bismuth, mercury, lead, and the alkaline earths.

The recent discovery of bismuthotantalite (*Min. Mag.*, 1929, **22**, 185), a mineral rich in bismuth and analogous to stibiotantalite, rendered a study of the separation of bismuth from the earth acids desirable. We proceeded as for the separation of antimony from the earth acids, the first bismuth sulphide precipitate (which always contained a little earth acid) being dissolved in sulphuric acid, the liquid treated with tartaric acid and excess of ammonia, and poured into ammonium sulphide. The re-precipitated sulphide was collected, dissolved in hot dilute nitric acid, and the bismuth determined by our modification of the phosphate method (ANALYST, 1920, **45**, 435). When igniting the sulphur globules, resulting from the nitric acid attack on the second bismuth sulphide, we invariably obtained a mgrm. (more or less) of residue which was identified as earth acid, and added to the main fraction. Hence, the process gives a more perfect separation with antimony than it does with metals the sulphides of which are insoluble in ammonium sulphide, such as bismuth and copper (*vide infra*).

C. COPPER AND EARTH ACIDS.—For the sake of uniformity in procedure, our tests with copper oxide were conducted in precisely the same manner as those with antimony and bismuth. The copper was, therefore, necessarily recovered in two fractions, the one soluble, the other insoluble, in ammonium polysulphide. The former was re-precipitated, like antimony sulphide, by boiling with acetic acid. The combined precipitates were dissolved in nitric acid, the solution evaporated, diluted, filtered, and electrolysed for copper, while the small sulphur residue was ignited, leaving, in each case, about 1 mgrm. of pentoxides.

D. THE SEPARATION.—For the separation of the hydrogen sulphide group metals from the earth acids we advocate the following process: The mineral (0·25 to 0·5 grm.), or the mixture of the oxides (about 0·2 grm. M_2O_5) is fused with 3 to 4 grms. of potassium bisulphate in a 50 c.c. silica crucible, and the resulting mass dissolved in tartaric acid or ammonium tartrate, as described in XIX (*loc. cit.*).

In the case of minerals, the acid solution is allowed to stand for an hour, then freed by filtration from the deposited stannic oxide, lead sulphate, silica and, possibly, unattacked mineral. If necessary, the fusion and lixiviation are repeated on the ignited residue, after previous extraction with ammonium acetate to remove lead sulphate, if present.

The clear liquid is treated at 60° C. with hydrogen sulphide, and left in a warm place for an hour to clear. The sulphide precipitate, SP^1, is collected, and washed with 2 per cent. sulphuric acid containing hydrogen sulphide; the filtrate is concentrated by evaporation.

Treatment of SP^1.—Filter and precipitate are returned to the beaker, and warmed with 8 c.c. of strong sulphuric acid, with repeated dropwise addition of nitric acid, till the organic matter is destroyed. The oxidant is completely expelled by strong heating. The mass, when cold, is treated with 10 c.c. of 20 per cent. tartaric acid solution and 25 c.c. of warm water. Ammonia in moderate excess is added, and the liquid poured slowly into fresh yellow ammonium sulphide; hydrogen sulphide is passed for a few minutes, and the beaker allowed to stand on a covered water-bath for an hour or more.

Treatment of SP^2.—If sulphides insoluble in ammonium sulphide (SP^2) have separated, they are collected, washed with dilute ammonium sulphide, and dissolved in hot dilute nitric acid, which is evaporated. The residue is taken up with dilute acid, and the solution filtered through a small paper, which is washed with dilute acid and transferred to a tared porcelain crucible *C*. The filtrate is analysed for bismuth and copper (traces of lead) by the usual methods.

SP^3.—The clear yellow ammonium sulphide solution (or filtrate from SP^2) is acidified with acetic acid, boiled, treated with hydrogen sulphide, and left to clear. The precipitate, SP^3, is collected and washed as before, and the filtrate concentrated by evaporation. SP^3 is returned to the beaker with the paper, heated with 10 c.c. of strong sulphuric acid and several grms. of potassium sulphate till the acid mass is perfectly colourless. After dilution and suitable acidification with hydrochloric acid the antimony is titrated with permanganate. The titrated liquor is treated with iron wire, and the precipitate examined for copper; the filtrate is tested with hydrogen sulphide for tin.

Earth-Acid Recovery.—The bulk of the earth acids is precipitated by tartaric hydrolysis as *HP* in the concentrated filtrate from SP^1; the filtrate from *HP* is added to that from SP^3, and the balance of the earth acids precipitated therefrom as *TP* (XIX, *loc. cit.*, C, E, F). The precipitate *TP* is strongly ignited in crucible *C*, containing the small residue from SP^2, then warmed with 1:1 hydrochloric acid till white (it is usually pink, being contaminated with a trace of iron), and collected on a 7 cm. filter. The precipitate, *HP*, is then ignited in the same crucible, leached with acidified water, and added to *TP*. The combined precipitates are strongly ignited in crucible *C*, and weighed; the ash of several filters has to be subtracted from the weight.

RESULTS OF TEST SEPARATIONS.—In every test analysis given below, the quantitative composition of the oxide mixture (in no case were the oxides fused and leached separately) was unknown to the operator. The two M_2O_5 fractions, *HP* and *TP*, are given separately, as we wish to record and briefly discuss the *HP*:*TP* ratio. The weight of *TP* includes any small recoveries of pentoxide from SP^2. (The figures represent grms.)

	Taken.		Found.	*HP.*	*TP.*	Found.	M_2O_5.	Sb_2O_3.
Exp.	M_2O_5.	Sb_2O_3.	Sb_2O_3.	Net.	Net.	M_2O_5.	Error.	Error.
Ta 1	0·2638	0·0238	0·0238	0·2356	0·0282	0·2638	0·0000	0·0000
,, 2	0·2022	0·0618	0·0616	0·1728	0·0291	0·2019	−0·0003	−0·0002
,, 3	0·1515	0·1266	0·1251	0·1263	0·0255	0·1518	+0·0003	−0·0015*
Nb 4	0·2169	0·0607	0·0614	0·1888	0·0276	0·2164	−0·0005	+0·0007
,, 5	0·1720	0·1152	0·1144	0·1471	0·0244	0·1715	−0·0005	−0·0008
		Bi_2O_3	Bi_2O_3					Bi_2O_3
Ta 6	0·1780	0·1024	0·1025	0·1365	0·0406	0·1771	−0·0009	+0·0001
,, 7	0·1370	0·1284	0·1271	0·0600	0·0770	0·1370	0·0000	−0·0013
,, 8	0·2002	0·0721	0·0722	0·1608	0·0389	0·1997	−0·0005	+0·0001
Nb 9	0·2089	0·1826	0·1834	0·1639	0·0455	0·2094	+0·0005	+0·0008
,, 10	0·1006	0·1497	0·1486	0·0720	0·0286	0·1006	0·0000	−0·0011
		CuO	CuO					CuO
Ta 11	0·1400	0·0592	0·0590	0·1285	0·0111	0·1396	−0·0004	−0·0002
Nb 12	0·2039	0·0675	0·0670	0·1728	0·0308	0·2036	−0·0003	−0·0005
EA 13	Taken:	M_2O_5	0·1504;	Sb_2O_3	0·0785;	Bi_2O_3	0·1012.	
	Found:	,,	0·1505;	,,	0·0780;	,,	0·1012.	

* *Exp.* 3: Sb_2S_3 filtered off too soon; proved minute amount of Sb in ignited *HP* by applying our method.

Ratio of HP to TP.—It will be observed that the proportion of earth acid recovered in these tests as *HP* by tartaric hydrolysis is much lower than that obtained in the earlier investigation of tartaric hydrolysis, where it was found that "precipitation is complete but for a few mgrms." (XVI, ANALYST, **1929**, **54**, 708). The explanation is, that the solutions submitted to tartaric hydrolysis in the present investigation contained more tartaric and sulphuric acids—necessarily introduced in the process of solution—than those tested in Section XVI, either acid causing less complete precipitation. The observation has a certain practical importance, and will be borne in mind when we apply our methods to the analysis of minerals.

The original procedure proposed by Schoeller and Powell for the separation of the earth acids from the hydrogen sulphide group is described in Hillebrand and Lundell's *Applied Inorganic Analysis* (ANALYST, 1930, **55**, 351), wherein it is stated that the method gave "perfect separations of antimony, tin, lead and copper, from solutions containing as much as 0·1 grm. each of Sb_2O_5 and Ta_2O_5" (p. 470, footnote 17). This statement is at variance with the observations recorded in this Section. That the metals of the hydrogen sulphide group are quantitatively precipitated is not questioned, but we repeat that the precipitate, in our experience, always carries a little earth acid; and we are of opinion that it should always be re-treated by the method described above.

SUMMARY.—The separation of tantalum and niobium from antimony, bismuth, and copper was studied. When the mixed oxides were fused with bisulphate, the mass dissolved in tartaric acid, and the clear solution treated with hydrogen sulphide, the sulphide precipitate was always found to be contaminated with a few mgrms. of earth acid. The co-precipitation is ascribed to hydrolytic decomposition of the tartaric earth-acid complexes. The separation is completed by further treatment of the sulphide precipitate; this is dissolved in strong sulphuric acid, tartaric acid and excess of ammonia are added, and the solution is poured into ammonium sulphide. Bismuth and copper sulphides are precipitated; the filtrate is acidified with acetic acid, giving a precipitate of antimony sulphide. The small fraction of earth acid occluded in the original sulphide precipitate is found in the filtrate from the antimony precipitate. Directions are given for the quantitative recovery of the earth acids.

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DISCUSSION

Dr. B. S. EVANS said that he had often had occasion to separate the hydrogen sulphide group from tantalum and niobium, and had so far to assume that the separation was fairly complete; now, of course, he must revise that. He was quite aware that tartaric acid complexes were unstable in acid solution; in fact, if one added excess of acid and boiled, one noticed that earth acids would come down, whereas the same did not occur with oxalic acid. He noticed that oxalo-complexes were precipitated by alkali, but not by acids. He wondered, therefore, if the separation were carried out in oxalic, instead of tartaric, solution, if the same occlusion of earth acid would take place. The only difficulty, presumably, would be tin, the sulphide of which was held in solution by oxalic acid; he was on the point of publishing a paper showing that stannous sulphide could be precipitated satisfactorily in alkaline oxalate solution. He strongly deprecated the use of ammonium sulphide for the separation of antimony from, for example, lead; antimony sulphide was certainly soluble in very strong ammonium sulphide, but the solution was uncertain and precarious. It did not seem to be widely known that one could precipitate antimony sulphide from its solution in sodium sulphide by the mere addition of ammonium chloride. He had good reasons for disliking ammonium sulphide separations altogether.

Dr. J. GRANT asked if Dr. Schoeller had had occasion to determine the optimum *p*H values at which hydroxides and sulphides precipitated. Most common metals had a definite *p*H range at which they were brought down, but there were no data available regarding niobium and tantalum, and he thought this would be very useful.

Dr. SCHOELLER, in reply, invited Dr. Evans to test sulphide precipitates, obtained from tartrate solutions containing earth acids, by the method described in the present paper. He was not prepared to say that such sulphide precipitates would invariably prove to occlude earth acid; but he thought it safest, in all accurate work, to re-treat the sulphides as described. He was fully aware that oxalo-complexes were more stable in acid solution than tartaro-complexes, but had refrained from using the former because oxalic acid prevented the precipitation of tin by hydrogen sulphide.

In reply to Dr. Grant's inquiry, he thought that the question of the *p*H values of solutions containing organic complexes of the earth acids was so involved that he and his collaborators had come to the conclusion that such measurements would not help them in their task. The determination of *p*H values was, no doubt, most useful in a study of the precipitation of sulphides and hydroxides of common metals from simple mineral acid solutions; but he and his collaborators were dealing with solutions containing much organic acid and soluble complexes of various amphoteric oxides, as well as salts and mineral acid. His personal feeling was that the *p*H value of such solutions, even if accurately known, was only one of several factors affecting the operations.

Methods for the Chemical Examination of Dyed Leathers for the Presence of Diamines and Aminophenols

BY F. E. HUMPHREYS, PH.D., A.R.C.S., A.I.C., AND
H. PHILLIPS, D.SC., F.I.C.

IN several cases of dermatitis, alleged to have been caused by dyed leather used for clothing and hat-bands, it has been found necessary to examine the leathers for the presence of para- and meta- diamines and aminophenols. These organic bases are not commonly used, as such, for the purpose of dyeing leather. They are, however, used in the manufacture of certain leather dyestuffs, and among leather dyers and users it has been assumed that traces of these compounds may pass unchanged through the dye-manufacturing process, and be present in the finished dyestuff.

Valuable tests for the detection of diamines and aminophenols in extracts of fur have been published by Cox (ANALYST, 1929, **54**, 694) and by Forster and Soyka (*J. Soc. Dyers and Colourists*, 1931, **67**, 99; ANALYST, 1931, **56**, 476). These and other tests have been applied to the detection of para- and meta- phenylenediamines in leather extracts by Callan and Strafford (ANALYST, 1931, **56**, 625), who found that some of them gave misleading information, owing to the presence of tannins in the extracts, and concluded that only a limited number of the tests were applicable. Even in these cases the result should be confirmed by applying the test to the leather extract after the addition of very small amounts of the suspected diamine.

The methods employed for dyeing and colouring clothing and hat-band leathers vary from factory to factory, and a large number of complex substances and mixtures are frequently applied to the leathers in order to fix the dyestuff and to obtain a special "finish." Extracts of such leathers may contain not only tannins, but also other complex substances derived from the fixing and finishing materials. For these reasons it will always be difficult to draw definite conclusions from tests made directly on leather extracts.

Methods have, therefore, been investigated, by which diamines and aminophenols may be recovered from leather and leather extracts, and thus obtained free from tannins and other substances liable to interfere with the tests. For this investigation specially treated leathers have been used. Known volumes of standard solutions of the hydrochlorides of diamines and aminophenols were applied to vegetable-tanned sheepskin leathers and dyed and undyed semichrome leathers (*i.e.* leathers which have been vegetable-tanned, stripped and re-tanned with chromium compounds), and the leathers allowed to dry in air. In this manner, samples of dyed and undyed leathers containing known amounts of the organic bases were obtained.

The tests used in the present investigation were those described by Cox (*loc. cit.*), and the additional tests suggested by Callan and Strafford (*loc. cit.*). The reagents employed were made up as described by Callan and Strafford; the volumes of these reagents used, irrespective of the concentration of the solution under examination, were as follows:

No. 1. *Nitrous Acid.*—To the solution 0·5 ml. of 2 *N* hydrochloric acid is added, followed by 0·5 ml. of 0·5 *N* sodium nitrite solution.

No. 2. To the mixture obtained in Test 1, 5·0 ml. of 0·05 *N* alkaline solution of β-naphthol are added.

No. 3. *Sodium Hypochlorite.*—To the solution, made faintly alkaline with 0·1 *N* sodium hydroxide solution, 1 ml. of dilute sodium hypochlorite solution is added.

No. 4. *Phenol and Hypochlorite.*—To the solution, made faintly alkaline with 0·1 *N* sodium hydroxide solution, 1 ml. of 5 per cent. phenol solution is added, followed by 2 to 5 drops of dilute sodium hypochlorite solution.

No. 5. *p-Dimethylaminobenzaldehyde.*—To the solution, acidified with 0·2 ml. of 2 *N* hydrochloric acid, 1 ml. of a 1 per cent. alcoholic solution of the reagent is added.

No. 6. *Ferric Chloride.*—To the neutral solution 1 drop of a 10 per cent. solution of ferric chloride is added.

No. 7. *Diazobenzene-p-sulphonic Acid.*—To the solution 1 grm. of sodium acetate crystals is added, followed by 1 ml. of 0·05 *N* diazobenzene-*p*-sulphonic acid solution.

No. 8. *Aniline and Dichromate.*—To the solution, acidified with 1 ml. of 2 *N* hydrochloric acid, 1 ml. of a 1 per cent. aniline hydrochloride solution is added, followed by 1 drop of 5 per cent. potassium dichromate solution.

The tests were carried out in Nessler cylinders, and the colorations obtained were compared with those given by solutions of diamines and aminophenols of known concentration. By this means the amount of the diamine or aminophenol which had been recovered from the sample of leather was determined approximately.

Attempts to determine the amount of harmful organic base present in extracts of leathers, alleged to have caused dermatitis, frequently revealed that it was impossible to match exactly the colorations obtained with very dilute solutions of diamines and aminophenols. Had these determinations not been attempted, the colorations might have been regarded as positive results. Further, it was found that some of these colorations could be accurately matched by using very dilute solutions of harmless bases.

The causes underlying the action of *p*-phenylenediamine and similar compounds on skin have been the subject of considerable discussion (Parsons, *Reports on Public Health and Medical Subjects*, 1924, No. 27; Cox, *loc. cit.*; Percival, *Lancet*, 1931, **221**, 417). Although the action of *p*-phenylenediamine has frequently been ascribed to semi-oxidised forms of the base, no reference has hitherto been made to the wide use of dimethyl-*p*-phenylenediamine and *p*-phenylenediamine for the study of the oxidation processes in animal and vegetable tissues. When placed in contact with such materials, dimethyl-*p*-phenylenediamine is oxidised to a reactive quinone-imine which condenses with naphthol, forming an indophenol blue, whilst *p*-phenylenediamine is probably converted into a quinone di-imine, which forms a purple compound, analogous to quinhydrone, by condensation with an unchanged molecule of diamine. Szent-Györgyi (*Biochem. Z.*, 1925, **157**, 79) found that this purple addition compound was reduced to a colourless compound (probably the diamine) by lactic acid, with the addition of washed muscle, and suggested that *p*-phenylenediamine could act as a carrier between the oxygen activators and dehydrogenases in the cell. These and other experimental results (Harrison, *Biochem. J.*, 1929, **23**, 982) suggest that the diffusion of *p*-phenylenediamine or its quinone di-imine into the cells of the skin might seriously affect their oxidation-reduction processes. Possibly such compounds can interfere with the functions of the cell-catalysts, and in this way divert or arrest some chain of vital reactions.

On the basis of this interpretation, it would appear that *p*-phenylenediamine and its partly oxidised products are equally obnoxious, and that the susceptibility of different people to the diamine may increase as the resistance of their skins to penetration by the diamine or its oxidation products decreases.

THE RECOVERY OF DIAMINES AND AMINOPHENOLS FROM SPECIALLY TREATED VEGETABLE-TANNED AND SEMICHROME CLOTHING LEATHERS

(*a*) *By Distillation in a Current of Super-heated Steam.*—Tannins and complex dyestuffs are not volatile in a current of super-heated steam, whereas a large number of dyestuff intermediates can be separated under these conditions. The distillate from a piece of leather containing dyestuff volatile intermediates, therefore, consists of a colourless, dilute solution of those intermediates.

The leather samples, prepared as described, were cut into small pieces, and these were placed in a flask, together with distilled water (75 ml.) and saturated sodium carbonate solution (2 ml.). A current of super-heated steam (200° C.) was passed into the boiling mixture until 250 ml. of distillate had been obtained. This was filtered, and aliquot portions (25 to 40 ml.) were then examined in Nessler cylinders by means of the tests enumerated on p. 291.

One serious objection can be raised to this method (see Cox, ANALYST, **1931, 56**, 633). It is possible that, under the combined influence of super-heated steam and decomposing leather, normally stable complex dyes might be reduced or resolved into intermediates. If this possibility is borne in mind, distillation in super-heated steam forms a useful preliminary method of examination.

In Table I the results obtained with the prepared leather samples are given. In the last column of this Table, the tests which were positive are recorded, the figures in brackets indicating the amount (in mgrms.) of the diamine or aminophenol found, and those printed in italics the test or tests by which the amounts were determined.

TABLE I

THE RECOVERY OF DIAMINES AND AMINOPHENOLS FROM LEATHERS BY MEANS OF SUPER-HEATED STEAM

Diamine or aminophenol.	Weight of diamine or aminophenol added to leather. Mgrms.	Nature of leather.	Weight of leather. Grms.	Positive tests given by:
p-Phenylenediamine	10·0	Vegetable-tanned sheepskin	20·0	4, 5, 8
,,	7·0	,, ,,	5·0	Nil
,,	7·5	,, ,,	7·5	4, *5*, 8 (0·15)
,,	5·0	,, ,,	8·3	4, 8
m-Phenylenediamine	5·0	Vegetable-tanned sheepskin	7·0	*1*, 7 (0·15)
,,	5·0	Dyed semichrome	6·5	*1*, 7 (0·10)
m-Toluylenediamine	5·0	Vegetable-tanned sheepskin	6·1	*1*, 4, 7 (0·60)
,,	5·0	Undyed semichrome	7·0	*1*, 7 (0·18)
,,	5·0	Dyed semichrome	5·7	*1*, 7 (0·06)
Metol	5·0	Vegetable-tanned sheepskin	4·2	4
,,	5·0	Dyed semichrome	6·3	*4* (0·06)
p-Aminophenol	5·0	Vegetable-tanned sheepskin	11·5	4, 6
,,	5·0	Dyed semichrome	6·0	4

Reliance cannot be placed on Test 4, because the steam distillate from a sample of leather, to which no diamines had been added, gave a blue coloration when this test was applied. The distillates from the leathers which had been treated with the *o*- and *m*-aminophenols and amidol failed to give distinctive reactions.

(*b*) *By the Continuous Extraction of Extracts of the Leather with Benzene.*—The samples of leather were extracted by two methods: by placing the leather (cut into small pieces) in 40 ml. of 1 per cent. acetic acid for 18 hours, or in 40 ml. of 0·1 *N* hydrochloric acid for 6 hours.

The extracts thus obtained were filtered, placed in a continuous extractor, and extracted with benzene for 24 hours. This extraction removed any benzene-soluble tannin substances, part of some aminophenols and *m*-diamines, but none of the other organic bases. Saturated sodium carbonate solution (5 ml.) was added to the leather extract, which was then re-extracted with fresh benzene for a further 24 hours. Finally, the leather extract was made strongly alkaline by the addition of 2 ml. of 40 per cent. sodium hydroxide solution, and again extracted with fresh benzene for 24 hours.

Each benzene extract thus obtained was evaporated to dryness under reduced pressure, after the addition of 0·5 ml. of *N* hydrochloric acid. The residues were dissolved in water, and the solutions obtained were filtered, and tested by the methods previously described. The results are summarised in Tables II and III, which are arranged on a similar plan to Table I. Five mgrms. of a diamine or aminophenol had been applied to each of the leather samples, which all had the same area (2 ins. by 10 ins.).

TABLE II

THE RECOVERY OF DIAMINES AND AMINOPHENOLS FROM SEMICHROME LEATHERS BY EXTRACTION WITH 1 PER CENT. ACETIC ACID

Diamine of aminophenol.	Leather. Weight. Grms.	Leather. Nature.	Benzene extract of acid extract of leather.	Benzene extract of acid extract of leather made alkaline with sodium carbonate.	Benzene extract of acid extract of leather made alkaline with sodium hydroxide.
			Positive reactions obtained:		
p-Phenylenediamine	8·2	Dyed	nil	*5*, 2, 4, 8 (0·10)	nil
m-Phenylenediamine	6·5	Dyed	—	nil	nil
,, ,,	7·7	Undyed	—	nil	nil
,, ,,	5·2	Undyed	1, 2 (trace)	—	—
m-Toluylenediamine	6·8	Undyed	nil	nil	nil
,, ,,	8·0	Dyed	nil	nil	nil
,, ,,	10·1	Dyed	nil	nil	nil
Metol	7·8	Undyed	nil	*4* (0·20)	nil
Amidol	6·2	Undyed	nil	nil	nil
o-Aminophenol	6·0	Undyed	1, 2, 6, *8* (0·20)	1, 4, *8* (0·20)	nil
m-Aminophenol	6·4	Undyed	*7* (0·06–0·10)	2, 4, 5, *7* (0·20)	nil
p-Aminophenol	5·8	Dyed	—	nil	nil
,,	6·0	Undyed	—	*4*, 6 (0·50)	nil

TABLE III

THE RECOVERY OF DIAMINES AND AMINOPHENOLS FROM UNDYED SEMICHROME LEATHERS BY EXTRACTION WITH 0·1 *N* HYDROCHLORIC ACID

Diamine of aminophenol.	Weight of leather. Grms.	Weight of diamine or amino-phenol. Mgrms.	Benzene extract of acid extract of leather.	Benzene extract of acid extract of leather made alkaline with sodium carbonate.	Benzene extract of acid extract of leather made alkaline with sodium hydroxide.
			Positive reactions obtained:		
p-Phenylenediamine	6·0	5·0	Faint coloration* given by 2, 5, 7	2, 4, *5*, 7, 9 (2·0)	2, 4, *5*, 8 (0·10)
m-Phenylenediamine	6·1	6·5	Faint coloration given by 7	1, 2, *7* (0·60)	Possible trace by 7
m-Toluylenediamine	6·2	6·5	2, *7* (0·03–0·06)	2, *7* (0·12)	Possible trace by 7
Metol	6·4	5·0	Faint coloration given by 2, 7	*4*, 7 (2·5)	*4* (0·3)
Amidol	6·3	6·5	Faint coloration given by 2, 7	Possible trace by 2	nil
o-Aminophenol	6·7	5·0	nil	nil	nil
m-Aminophenol	6·6	5·5	*2*, 4, 5, 7 (0·3)	2, *7* (0·25)	nil
p-Aminophenol	6·5	5·5	Faint coloration given by 4	*4* (less than 0·05)	nil
Nil	6·8	nil	Faint coloration given by 2, 7	Faint coloration given by 2, 7	Faint coloration given by 2, 4

* "Faint colorations" were colorations which could not be matched by using very dilute solutions of the diamines and aminophenols in question.

From Table II it will be seen that, under the experimental conditions employed, *p*-phenylenediamine, metol, *o*-, *m*- and *p*-aminophenols are extracted from leather by 1 per cent. acetic acid. The *m*-diamines, however, are not readily extracted by this solvent; the results show that only a trace of *m*-phenylenediamine was extracted, whilst the amount of *m*-toluylenediamine extracted was so small that it could not be determined. As can be seen from Table III, 0·1 *N* hydrochloric acid extracts far larger amounts of these diamines, although, like acetic acid, it removes the *p*-diamine more readily than the *m*-diamines. Hydrochloric acid of the concentration employed is not such a good extracting agent for the *o*-aminophenol as 1 per cent. acetic acid.

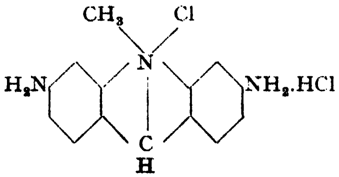
In conclusion, we wish to thank the Council of the British Leather Manufacturers' Research Association for permission to publish this paper.

LABORATORIES OF THE BRITISH LEATHER
MANUFACTURERS' RESEARCH ASSOCIATION.

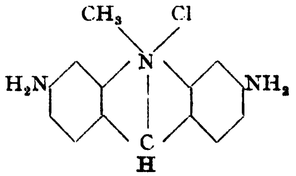
Note on the Recognition and Determination of the Flavines

BY P. J. UDALL, PH.D., A.I.C.

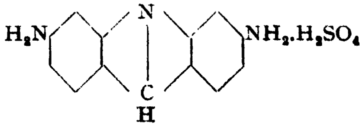
INTRODUCTION.—Since the discovery of acriflavine by Benda (*Ber.*, 1912, **45**, 1787; *cf.* also Cassella & Co., D.R.P. 243085) this interesting compound, together with euflavine and proflavine, has been the subject of a considerable amount of research. The three "flavines" are all derivatives of diamino-acridine, and their antiseptic properties have been studied by many workers (*cf.*, for example, Browning and co-workers, *Brit. Med. J.*, 1917, 73; Browning and Gulbransen, *Proc. Roy. Soc.*, 1918, (A), **90**, 136; Bohland, *Deut. Med. Wochenschr.*, 1919, **45**, 797; Zell, *Amer. J. Vet. Med.*, 1920, **15**, 144; Lenz, *Z. ges. exp. Med.*, **12**, 195; Smith, *J. Pharm. Expt. Ther.*, 1923, **20**, 419), and it is obvious that the identification of these compounds, and their differentiation from other yellow dyestuffs, are of some importance when they are used for antiseptic dressings. They have the following constitutional formulae :



Acriflavine
($C_{14}H_{14}N_3Cl.HCl$).



Euflavine
($C_{14}H_{14}N_3Cl$).



Proflavine
($C_{13}H_{11}N_3.H_2SO_4$).

IDENTIFICATION OF THE PURE COMPOUNDS.—Tests have been carried out with the object of studying the effect of various reagents on the "flavines," and the results are tabulated below.

Reagent	Flavine		
	Acriflavine	Euflavine	Proflavine
	—	—	—
Concentrated sulphuric acid.	Green-yellow fluorescence. Evolution of HCl.	Green-yellow fluorescence. Evolution of HCl.	Green-yellow fluorescence.
Dilution of above solution.	Brilliant orange-red colour and fluorescence.	Brilliant orange-red colour and fluorescence.	Brilliant orange-red colour and precipitate.
Sodium hydroxide solution.	Yellow colour and precipitate. No fluorescence.	Yellow colour and precipitate. No fluorescence.	With excess reagent deposit of pale yellow needles.
Concentrated hydrochloric acid.	Reddish colour. No fluorescence.	Reddish colour. No fluorescence.	Reddish colour. No fluorescence.
Concentrated nitric acid.	Crimson lake colour.	Crimson lake colour.	Reddish colour. Slight fluorescence.
Dilute hydrochloric acid and potassium nitrite.	Violet colour.	Violet colour.	Violet colour.

To ascertain whether these "flavines," as a class, could readily be distinguished from common yellow dyestuffs of various types, the following dyes were subjected to the above tests:—Metanil Yellow; Paramine Khaki 20045; Dianol Fast Yellow ARX, Dianol Fast Orange D, Citronine Y conc., Titan Yellow G, Spirit Yellow 81451 and Eosin. Phenyl acridine, a substance of the same family as the "flavines," was also included. All the substances examined were readily distinguished from the "flavines" by the above reactions, from which it may be concluded that if, for any reason, a yellow dye not of the flavine type were used, there should be no great difficulty in detecting the substitution.

It will be seen that acriflavine and euflavine cannot be distinguished by these tests. Proflavine, however, may be recognised by its reaction with aqueous caustic soda, and also by the behaviour of its solution in strong sulphuric acid on dilution. Further, a definite precipitate is obtained with barium chloride solution—a reaction not given by either acriflavine or euflavine.

Acriflavine might be expected to yield a precipitate of silver chloride on treatment with silver nitrate in aqueous solution, but actually only a very faint turbidity is obtained, which cannot be looked upon as conclusive. It is stated in a recent paper (Howes, *Ind. Eng. Chem.*, *Anal. Edit.*, **1930**, **2**, 114) that acriflavine liberates carbon dioxide from saturated sodium bicarbonate solution. The reaction was found to be satisfactorily definite when solid acriflavine was used, but with aqueous solutions it was very difficult to detect evolution of gas.

To summarise these qualitative experiments, it will be seen that the "flavines" are readily distinguished from yellow dyestuffs of other types, and that proflavine gives certain characteristic reactions. Differentiation between euflavine and acriflavine would be desirable, and, since the qualitative reactions studied evidently fail to distinguish between these very similar compounds, it was concluded that quantitative methods would have to be employed.

Various quantitative methods may be utilised to differentiate between acriflavine and euflavine in the pure state, *viz.* determination of carbon and hydrogen by the usual combustion method; determination of nitrogen; determination of amino group; determination of chlorine.

Kjeldahl's method may be used for the nitrogen determination. The amino group determination requires a more detailed explanation, as an external indicator must be used, and recognition of the end-point of the titration is a matter of some delicacy.

Standard potassium or sodium nitrite is prepared so that its strength is such that 1 c.c. = 0·01 grm. to 0·02 grm. of euflavine. Control experiments with pure euflavine have indicated that only one amino group takes part in the reaction. The standard nitrite solution is, therefore, prepared on this basis. The above limits to the strength of the solution are necessary, as it must be remembered that the "flavines" are used in very low concentrations, of the order of 1 in 500 and less. If the strength of the nitrite solution is outside the above-mentioned limits, either the amount of nitrite solution used will be very small, so that experimental error becomes proportionally large, or the end-point of the titration will be very indefinite.

A suitable weight of the flavine is dissolved in water (or a convenient volume of the liquid is taken, if a solution is under examination), excess of hydrochloric acid is added, the whole is cooled to 0° C. in a freezing mixture, and titrated with the standard nitrite solution, starch-iodide paper being used as indicator. The mixture must be constantly stirred throughout the titration. The end-point is reached when the bluish coloration (which is seen immediately after the liquid has soaked into the paper) persists for several seconds. Concordant results have been obtained by this method, when using 0·01 grm. of euflavine for each titration.

IDENTIFICATION OF ANTISEPTIC IN IMPREGNATED DRESSINGS.—The determination of the nature of the antiseptic on a cotton fabric presents some difficulty. Usually the amount of the antiseptic is extremely small, and interference from impurities in the cotton may be serious.

The presence of a "flavine" on the fabric may be established by extracting the material with a suitable solvent (ethyl alcohol or water) in a large Soxhlet apparatus, removing the solvent, and subjecting the residue to the qualitative tests outlined above. Adulterants will readily be recognised; proflavine is detected by the reactions with barium chloride and caustic soda, but acriflavine and euflavine cannot be distinguished from one another. It would appear necessary, therefore, to have recourse to quantitative methods.

It is obvious that some material may be extracted from the cotton by the solvent used, and in practice this has been confirmed, cotton dressings impregnated with 0·1 per cent. of euflavine yielding extracts amounting to 0·2 to 0·4 per cent. If the extract be now subjected to quantitative investigation, difficulties arise. The combustion methods cannot be employed, owing to the impure state of the extract, which it appears impossible to purify from material extractable from the cotton.

The Kjeldahl method is suitable, provided that no nitrogenous matter is removed from the cotton by the solvent. Raw cotton contains a small amount of albuminous matter, usually equivalent to 0·3 to 0·7 per cent. of nitrogen. This is practically completely removed when the raw cotton is bleached, and purified cotton fibre consists of nearly pure cellulose (Knecht and Hall, *J. Soc. Dyers & Col.*, 1918, **34**, 220). One would not expect, therefore, to find an appreciable amount of nitrogen in highly-purified cotton to be used for medical dressings. As was to be expected, a blank determination, carried out on medical gauze, yielded no nitrogen.

In experiments with cotton gauze impregnated with euflavine, the nitrogen found corresponded with the amount of antiseptic on the fabric, two consecutive determinations giving identical results of 0·5 per cent. euflavine. It should be noted, however, that the result may be calculated as either euflavine or acriflavine.

Determinations of the chlorine content of extracts derived from impregnated dressings gave discordant results. As there is always a small amount of mineral matter present, even in highly purified cotton, it is possible that some chlorine is derived from this inorganic material. The amounts of chlorine in acriflavine and euflavine are 13·7 per cent. and 24 per cent., respectively, and it will be seen that a very small amount of inorganic chloride is sufficient to introduce a serious error when the chlorine is calculated as euflavine or acriflavine. Thus 0·056 per cent. of sodium chloride would be returned as 0·25 per cent. of euflavine, even though no euflavine had been added to the fabric. Mention should also be made of the fact that the "flavines" always contain a very small amount of mineral matter (Warren, *Repts. Lab. Amer. Med. Assoc.*, 1919, **12**, 64; 1921, **14**, 58). A determination of the amount of chlorine in a sample of pure acriflavine gave $Cl = 24{\cdot}4$ per cent.; the formula $C_{14}H_{15}N_3Cl_2$ requires 24·0 per cent. of chlorine. This method, therefore, is not suitable when applied to impregnated dressings.

The method depending upon the determination of amino group may be applied to impregnated gauze, as there are no impurities present which affect the titration. The gauze is extracted with a solvent (ethyl alcohol has been found to be the most suitable) in a Soxhlet apparatus until the fabric is practically colourless, and, after evaporation, the residue is taken up with excess of dilute hydrochloric acid, warmed on the water-bath, with stirring, for about fifteen minutes and cooled to 0° C., and the titration is carried out as previously described. Concordant results may be obtained by this method; typical figures obtained, using gauzes containing 0·1 per cent. of euflavine, are as follows:—0·08, 0·09, 0·09, 0·10, 0·10 (mean 0·09) per cent. of euflavine.

In the course of the work described in this paper it was noticed that reactions appeared to take place when euflavine was treated with bromine or iodine. In the case of bromine, a brilliant red compound is formed, and it appears that six atoms of bromine replace six atoms of hydrogen in the euflavine molecule. This conclusion was drawn from the results of titration experiments, and I have worked out a quantitative method for the determination of euflavine or acriflavine, but the conditions are extremely rigid, and the method is not suitable for the rapid determination of euflavine. It is hoped to communicate these results in a further paper. The red compound has not yet been quantitatively examined, but its reactions with certain reagents show a marked difference between euflavine and the brominated derivative.

Concentrated sulphuric acid.	Red coloration, becoming yellow on dilution.
Concentrated nitric acid.	Green coloration, becoming very pale orange on dilution.
Concentrated hydrochloric acid.	Yellow coloration.
Nitrous acid.	Yellow coloration, changing to dark red.
Hydrogen sulphide and ferric chloride.	Orange red coloration and precipitate.
Caustic soda solution.	Maroon coloration.

The reaction of euflavine with iodine is more complex, and a simple substance does not apparently result. Titration experiments indicate that four atoms of iodine react with one molecule of euflavine, yielding a brown-black substance.

SUMMARY.—1. The three "flavines" may be recognised and distinguished from other yellow compounds by the application of certain reagents, and proflavine may be readily distinguished by means of simple reactions.

2. Samples of "pure" acriflavine or euflavine can be differentiated by determining the percentage of carbon and hydrogen, nitrogen, chlorine or amino group.

3. Having limited the nature of the antiseptic on an impregnated gauze by qualitative methods, the amount can be determined accurately by means of the nitrogen or amino group methods, the results being expressible either as euflavine or acriflavine.

4. The amount of euflavine or acriflavine on an impregnated gauze cannot be found by determination of the amount of chlorine, owing to interference from impurities in the cotton.

5. Euflavine reacts with bromine and iodine; a red compound is formed, as a result of the reaction with bromine, and certain qualitative colour reactions of this compound are described.

I wish to thank Mr. W. L. Baillie, F.I.C., for his helpful advice.

DEPARTMENT OF THE WAR DEPARTMENT CHEMIST,
WOOLWICH, S.E.18.

Analyses of Two Samples of Irish "Bog Butter"

BY P. S. ARUP, M.Sc., F.I.C.

THESE samples were found buried in the peat, one in Co. Leitrim, wrapped in a skin, and the other in Co. Tyrone, contained in a tub with perforated wooden handles. Such samples have been found, not only in Ireland, but also in Iceland and Finland. The analyses recorded here were undertaken, as there are not many modern data available in connection with this material, while the results offer some features of interest to the analyst concerned with butter analysis.*

Radcliffe and Maddocks (*J. Soc. Chem. Ind.*, 1907, **26**, 3) published the analyses of two samples of bog butter (one of which was due to Hart); figures from these analyses have been included in the Table below, for comparison.

The two samples which I have examined were grayish-white in colour, showing a few small specks of the original butter yellow in the interior. They were brittle and waxy, giving the impression of porosity, and smelled like rancid tallow. The specific gravity of the samples was 0·72; after melting, stirring and resolidifying, the sp.gr. had increased to 0·84, showing that the material had contained gas, no doubt of bacterial origin. The analyses were as follows:

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* The desire to preserve the valuable nutritive constituents of milk in an edible form for use in seasons of scarcity can readily be understood, and different peoples appear to have solved the problem in different ways. Thus Marco Polo tells us of the dried milk of the Tartars, while from the writings of Pliny, Columella and other ancient authors, we gather that in their time cheese-making was already a highly-developed art among the Mediterranean peoples, while butter-making was practised by the Scythians and Germans, but not by the Southern peoples.

For purposes of preservation for any length of time, conversion into cheese is obviously a superior process to that of conversion into butter, and it is, therefore, not surprising to find that the custom of burying butter only persisted until comparatively recent times in those countries into which Mediterranean influence penetrated most slowly. The many difficulties attendant on the distribution of foodstuffs in former times undoubtedly enforced what must seem to us a considerable degree of tolerance of rancid and highly flavoured diet. There is even some evidence that a taste was developed for rancidity in butter; the Romans are said to have kept their butter until a certain degree of rancidity was produced; W. R. Wilde (*Proc. Royal Irish Academy*, 1856, **6**, 356) quotes as follows from Butler's *Hudibras*:

"Butter to eat with their hog,
Was seven years buried in a bog."

The archaeology of bog butter is dealt with in the above-mentioned paper, and in a communication to the *Irish Times* of May 16th, 1929, by Mr. Gogan, of the National Museum of Ireland, to whom I am indebted for the following information. A certain sample found in Tirnakill Bog, Co. Galway, was contained in a vessel dated 1789. It is probable that the practice of burying butter ceased in Ireland about the end of the eighteenth century, and that many of the specimens which have been found are of far greater antiquity, say, from the eleventh to the fourteenth century, the age of the older specimens being approximately determined by pyrographic decorations on the containing vessels. A certain estimate of age can also be deduced in some cases from the depth at which the specimen was found. No samples containing salt have ever been found.

From the large number of specimens found, some of which weigh as much as about 100 lbs., it would seem that the burying of butter must have been a widespread custom in Ireland.

	Leitrim.	Tyrone.	Radcliffe and Maddocks.	Hart.
Water, per cent.	1·54	1·10	—	46·3
Curd, per cent.	1·31	1·64	1·97	0·32
"Casein" (from Kjeldahl result), per cent. ..	0·37	0·16	—	—
Ash, per cent.	0·10	0·29	—	—
Salt	nil	nil	nil	nil
Characteristics of fatty matter.				
Reichert–Meissl value	0·6	0·45	1·2	1·4
Polenske value	0·65	0·75		
Iodine value	9·2	9·1	10·9	14·1
Acid value	190·7	196·9	201·9	—
Mean molecular weight of acids	294·2	284·9	—	—
Acetyl value	20·7	10·1	2·2	—
Melting point, °C.	45·6	47·9	48·0	44
Unsaponifiable matter, per cent.	0·65	0·58	—	—

The figures for "curd" represent non-fatty solids, and those for "casein" the nitrogen calculated as milk proteins (N multiplied by 6·39); they naturally do not represent these substances as ordinarily known; the very low "casein" in proportion to "curd" indicates loss of nitrogen. The high ash of the Tyrone sample is due to an abnormally high content of iron oxide, probably introduced by percolating water. Absence of salt seems to be a characteristic of all specimens of bog butter hitherto examined; it is not certain that they were made without salt, as this may have been removed by percolating water.

The fatty matter of the Leitrim and Tyrone samples had been completely hydrolysed to fatty acids. Fat hydrolysis in butter may be accomplished by two distinct groups of organisms, *i.e.* moulds belonging to the *Oidium*, *Penicillium* or *Cladosporium* orders, or by certain water bacteria, notably *B. fluorescens liquefaciens* or *B. prodigiosus*. The moulds consume part of the free fatty acids thus produced, notably the lower members, while the bacteria are eventually destroyed by the acids they liberate (Orla Jensen, *Dairy Bacteriology*, 1931, pp. 132 and 133, and Fierz David, *Z. angew. Chem.*, 1925, **1**, 6). In the case of small samples of butter, which expose relatively large surfaces to air, it is practically certain that the moulds will obtain predominance as typically aerobic organisms, which explains why hydrolysis is so often accompanied by a fall in the Reichert–Meissl value, as I showed to be the case with some old butter samples (ANALYST, 1929, **54**, 736), in which there was a certain quantitative parallel between the two processes.

In the four bog butters mentioned in the table, the soluble fatty acids had almost completely disappeared. This effect may have been largely due to the combined action of the fat-hydrolysing bacteria and the solvent action of percolating water, which would continuously remove excess of soluble acid and also introduce fresh bacteria.

The insoluble volatile (Polenske) acids were solid and powdery. They were probably largely derived from the oxidation of the unsaturated acids. Decidedly rancid butter fats often yield waxy solid insoluble volatile acids.

The low iodine values may be attributed to the chemical oxidation of the unsaturated fatty acids, as apart from the action of micro-organisms. A certain diminution of this value may be expected in all fatty material which has been kept for a long time, unless excluded from oxygen; the present cases are, of course, of an extreme order.

The mean molecular weights of the acids are high, compared with the figures to be expected from the acids derived from fresh butter; for the Tyrone sample the figure approximates to the molecular weight of stearic acid (284·3), whilst for the Leitrim sample it is considerably higher. The disappearance of the lower acids is in itself not sufficient cause to explain this, and it is probable that hydroxy derivatives of the higher acids have been formed by oxidation. This supposition is supported by the fact that the acids from the Leitrim sample had the higher acetyl value.

From the unsaponifiable matter of both samples, characteristic crystals of cholesteryl acetate (m.pt., 115° C.), were obtained by the digitonin method, with one recrystallisation. The fact that the cholesterol has not been altered or consumed in these extremely old samples, indicates that, so far as this constituent is concerned, the phytosteryl acetate test may be relied on when applied to any such old samples as the analyst is likely to meet with.

I wish to thank Mr. R. Harvey, late Inspector under the Irish Land Commission, for presenting the samples for analysis, and the Department of Agriculture, Irish Free State, for permission to publish the results.

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The Antimony Trichloride Colour Test for Cod-Liver Oil

In January, 1930, the Pharmacopoeia Commission appointed a Cod-liver Oil Colour Test Sub-Committee consisting of the following members:—J. H. Burn (Chairman), A. L. Bacharach, F. H. Carr, T. T. Cocking, N. Evers, H. A. D. Jowett, O. Rosenheim, and P. W. Tainsh.

The Sub-Committee was appointed to recommend a form of test for cod-liver oil, depending on what is known as the antimony trichloride reaction. In appointing the Sub-Committee, the Commission wished it to be understood that the inclusion of such a test in the Pharmacopoeia was not to be taken as necessarily indicating that the test afforded a measure of vitamin *A* content. The test, if included, might prove of value for indicating a limit of deterioration, or as indicating a characteristic property of cod-liver oil.

The Sub-Committee reported in March, 1931, and the Report was published by the Pharmacopoeia Commission. It was not found possible to include within the limits of this brief formal report to the Commission any account of the experimental work upon which the recommendations of the Sub-Committee were based. The following account is now published, in the hope that it will be of interest and value to other workers in this field.

Several modifications of the details of the antimony trichloride test, first proposed by Carr and Price, had been suggested from time to time, but no attempt had been made to show that, even by adherence to any one form of the test, the same results were yielded in the hands of different workers. The Sub-Committee set out to investigate the test, and to decide the conditions best calculated to give uniform results.

The Sub-Committee commenced their enquiry into the test by adopting, provisionally, conditions for its performance, based on the work of several workers, in general use at the time. They circulated the method and a number of samples of cod-liver oil to several chemists who had had considerable previous experience with the test. In some cases, these chemists arranged for additional observers in their laboratories to take readings for the purpose of comparison.

By proceeding in this way the Sub-Committee were at a great advantage over early investigators of the test, inasmuch as they were in a position to compare results obtained with the same sample of oil by a number of independent observers working under varying conditions.

The first results showed wide discrepancies. Three samples of oil ("A," "B," and "C"), distributed to four laboratories, showed the following variations:—"A," 6·5 to 10·1; "B," 4·5 to 6·1; "C," 9·7 to 15·2.

The necessity to investigate each stage of the test was, therefore, at once evident, and for the purpose two additional laboratories, with their staffs, were enlisted in the enquiry.

It became clear, after discussion, that the conditions for preparation of the antimony trichloride reagent, its concentration and method of storage, required closely defining if concordant results were to be obtained. The effects of variations in the reagent were carefully studied.

1. Effect of Concentration.—It was found that, with the same sample of oil and the same temperature for the test, a reduction in the concentration of the antimony trichloride reagent led to lower values being obtained; thus, at 20° C. the following table shows the results obtained with varying concentrations of antimony trichloride in B.P. chloroform:

Antimony trichloride, per cent.	29·0	26·9	25·1	23·1	21·0	19·0	17·0	15·1
Blue values	6·0	5·9	5·7	5·5	5·1	4·8	4·3	3·8

On the other hand, by carrying out observations at different temperatures, using, in each case, antimony trichloride solution, saturated at the respective temperatures of the tests, it was found that maximum and identical values resulted. The blue colour was, however, more fugitive and difficult to match when solutions of antimony trichloride of appreciably higher concentrations than 23·5 per cent. were employed.

2. Presence of Alcohol in the Chloroform used as Solvent of the Antimony Trichloride.—It was found that the presence of small percentages of alcohol in the chloroform employed as solvent of the antimony trichloride had a marked effect in increasing the solubility of the latter. In consequence, saturated solutions prepared by the different workers varied widely in strength, depending upon the alcohol content of the chloroform which they employed. The concentrations of antimony trichloride, saturated at 20° C. in pure dry chloroform

and in chloroform containing varying increasing amounts of alcohol, were found to be as follows:

Dry chloroform ..	23 per cent. w/v of antimony trichloride
With 1 per cent. of alcohol ..	38 „ „ „ „ „ „
„ 2 „ „ „ „ ..	50 „ „ „ „ „ „
„ 5 „ „ „ „ ..	80 „ „ „ „ „ „

Further, it was found that the presence of alcohol in the chloroform used for preparing the reagent had the effect of increasing the rate at which the colour faded, and thus added to the difficulties of ascertaining the maximum blue colour value. When, however, dry chloroform, free from alcohol, was used to prepare a solution of antimony trichloride saturated at 20° C., far more uniform results were obtained by all the workers for blue values, and also for the assay of the reagent by titration in verifying its content of antimony trichloride. Results of the assay of the reagent agreed closely, the mean figure of 25 determinations being 22·2 per cent. w/v of antimony trichloride, with extreme limits of 22·1 and 24·6 per cent.

Reagents prepared by the five workers were employed by each of them in testing two oils, and, except in the case of one worker, their results were in good agreement. For No. 1 oil the average of 20 observers was 6·2, with extreme limits of 5·5 and 6·9; and for No. 2 oil the average was 8·5, with extreme limits of 7·1 and 9·5.

Following the direction to use alcohol-free and dry chloroform in the preparation of the reagent, it was found by one worker that varying results were obtained by the use of chloroform which had undergone slight decomposition. Consequently, in the final details of the test, care was taken to prevent the use of decomposed chloroform by including the method of preparation of pure chloroform from the B.P. product. Although decomposition may take place in pure chloroform on storage, no indication was obtained of any deterioration occurring in the reagent over a reasonable period. The Sub-Committee ultimately recommended the following method for the preparation of the antimony trichloride reagent:

ANTIMONY TRICHLORIDE REAGENT.—A solution of antimony trichloride in pure dry chloroform, saturated at 20° C., is prepared in the following way:—Wash the chloroform two or three times with its own volume of distilled water, dry the chloroform over anhydrous potassium carbonate; pour off and distil, rejecting the first 10 per cent. of the distillate. During drying and distillation protect the chloroform from light. Wash antimony trichloride with the pure dry chloroform until the washings are clear. Prepare a solution, saturated at 20° C., of the washed antimony trichloride in the pure dry chloroform. The solution, which must contain not less than 21, and not more than 23 per cent. w/v of antimony trichloride, should be kept in a well-stoppered bottle of amber-coloured glass. *Assay.*—Mix 1 ml. with a solution of 2 grms. of sodium potassium tartrate in 20 ml. of water; rotate the mixture, add 2 grms. of sodium bicarbonate, and titrate with *N*/10 iodine. Each ml. of *N*/10 iodine is equivalent to 0·01141 grm. of antimony trichloride.

OTHER DETAILS OF THE TEST.—Having attained agreement regarding the reagent, the Sub-Committee then gave their attention to other details of the test.

It was found unnecessary to employ specially purified chloroform for preparing the solution of the oil for the test, since only 0·2 c.c. of this solution is required, whereas 2 c.c. of the reagent are directed to be used. Chloroform B.P. was, therefore, recommended for dissolving the oil, which was required to be weighed and not measured, thus ensuring greater precision.

Standardisation of Lovibond Glasses.—It was decided to measure the colour produced in the test through a colourless, rectangular glass cell of 10 mm. internal measurement, placed in a colorimeter designed for matching the colour of the solution, against colour glasses calibrated on the Lovibond scale. It was, therefore, considered desirable to check the uniformity of the standard blue glasses of a stated value of 5 units possessed by the different workers. For this purpose a specimen of the same blue glass was supplied to each worker for independent measurement against his glasses. The average of the mean values obtained by 30 observers was 4·93, and the mean figures of each observer differed from 4·93 by less than 0·1.

Source and Quality of Light.—The source and quality of the light used for illuminating the tintometer in the different laboratories were considered. The employment of "daylight" lamps was also investigated, but it was found that these varied so much in the quality of light emitted, even among lamps of the same brand, that it was not thought desirable to recommend them specifically for the particular purpose. It was agreed, however, that any source of light that would allow of an accuracy of reading within 0·1 unit might be used.

Effect of Method of Mixing.—The details of the technique to be adopted in adding the antimony trichloride reagent to the solution of oil were laid down, and it was decided not to specify any fixed interval before taking readings, as it was found that oils varied in their rate of colour development and subsequent fading. It was agreed that the value to be recorded was that corresponding to the maximum intensity of the blue component of the colour.

Effect of Dilution.—In order that the results by the different workers should be as comparable as possible with the different oils examined, it was required that the dilution of the oils should be such as to give an actual reading of close to 5 units. It was found that the majority of the observers showed the best agreement at about that value.

The necessity to employ red, yellow and neutral tint glasses in obtaining a colour match varied among the different observers.

The Influence of the Concentration of the Oil.—It has been shown by several observers that the graph relating the blue colour to the concentration of oil in the solution used for the test is not a straight line, but that the blue value diminishes with increasing concentration of the oil. This factor was, to some extent, responsible for the differences recorded between different observers in some of the earlier comparisons.

Since oils of widely different blue values cannot be compared in the same concentrations, because of the limited range within which it is possible to obtain accurate readings of the blue colour, it follows that any quantitative comparison of the blue values of such oils is fallacious.

Application of the Test to Unsaponifiable Matter.—The application of the test to the unsaponifiable matter, instead of directly to the oil itself, was considered by the Sub-Committee. A method was communicated to the Sub-Committee by Smith and Hazley, and subsequently published in The Analyst (**1931**, **56**, 265), by which the unsaponifiable matter could be readily prepared without loss of blue value. It has been shown (Church and Norris, *J. Biol. Chem.*, 1930, **87**, 139) that when the test is so applied the graph relating the blue colour to the concentration of the oil is practically a straight line, and that the errors due to differences in concentration are thus avoided. It has also been shown (Coward *et al.*, *Biochem. J.*, 1931, **25**, 1102; Analyst, 1931, **56**, 821) that the blue values obtained on the unsaponifiable matter show a better relationship to the biological values of the oils in vitamin *A*. It was decided, however, that, since the test to be recommended was merely a limit test, and since one fixed concentration of oil would be used in carrying out the test, the introduction of the further complication of preparing the unsaponifiable matter was not warranted.

Temperature.—In the earlier tests it was found that the colour was more permanent if the reading was taken at as low a temperature as possible, but, with the adoption of a solution of antimony trichloride saturated at 20° C., lower temperatures could not be used, as the reagent quickly becomes cloudy, even at a few degrees below 20° C. Moreover, there are practical difficulties in taking readings much below the temperature of the laboratory.

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This test was introduced in 1926 by Carr and Price, who found that, with antimony trichloride in chloroform solution, vitamin *A* gives a blue coloration, which persists for several minutes, and may be matched against standard blue glasses in a Lovibond tintometer. The readings thus obtained on two samples of cod-liver oil were found to agree approximately with the contents of vitamin *A* in the samples, as determined by feeding experiments.

As a result of subsequent work by a large number of investigators, some difference of opinion exists as to the value of the test as an indicator of the vitamin *A* content of cod-liver oils. Consideration of the evidence available renders it probable, however, that, provided that the test is carried out under carefully specified conditions, rough parallelism exists between the results of the Carr-Price test and those of biological tests. At the same time, there seems no doubt that the blue colour obtained in the reaction with antimony chloride is the resultant of various colours which may be due to various constituents of the oil, and that these constituents may vary, at least as regards their proportions, in different samples of cod-liver oil. Moreover, the possibility of the presence in certain cod-liver oils of components which interfere with the coloration appears to have been proved by a number of independent investigations. It seems probable that a more satisfactory correlation between biological activity and the colour value of an oil may be obtained if the unsaponifiable fractions of the oils, instead of the oils themselves, are subjected to the test.

T. H. P.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

OILED WRAPS FOR APPLES

THE storage of apples in "gas" stores has now assumed importance, for each year the number of these stores increases. The main principles involved in this storage are that advantage is taken of the carbon dioxide evolved by apples, so that an atmosphere is created which contains a minimum of 10 per cent. of carbon dioxide, and a temperature of about 42° F. is maintained. When the concentration of carbon dioxide becomes excessive, the gas must be allowed to escape, but, in case of a leak apparatus is provided for the chemical production of carbon dioxide.

Heavy losses of apples so stored are apt to occur from "scald," unless the apples are enclosed in oiled wraps. These oiled wraps consist of paper squares, impregnated with a medicinal paraffin, and they must not be confused with waxed wraps, for the latter are useless for wrapping gas-stored apples. The use of these wraps was first advocated in America, the discovery having been made, apparently, through the trial of a large number of substances. But the minimum amount of oil which these wraps should contain has never been determined, either experimentally or in practice, though the amount is invariably stated as 18 per cent. It is not quite clear whether the 18 per cent. alludes to the finished wraps, or whether 18 per cent. of oil should be added to the untreated paper. If 18 per cent. of oil is added to paper, the final paper should contain 15·2 per cent. I have examined several different consignments of American wraps, and I have found the amount of oil to vary from 11·5 to 14·9 per cent. These wraps have all been used with success. In their manufacture, oil is probably sprayed on to paper, and wraps in a consignment, or even in a package, show a considerable variation in oil content. If single sheets be examined from a package of about 300 wraps, a variation in oil content of about 1·5 per cent. may be found, but, if six one-half sheets of paper be taken, the variation is limited to about 0·5 per cent.

For the determination of oil, six one-half sheets of paper were usually extracted with petroleum spirit for two hours in a Soxhlet apparatus, after which the papers were air-dried, re-folded, and re-extracted for a further two hours. Similar figures are obtained if ether be substituted for petroleum spirit.

I have found the oil content of bundles of wraps to remain constant for three months, and I have little doubt that this constancy would be maintained for a much longer period, provided that no oil has exuded.

The rate of loss of oil, however, in wraps used for the wrapping of apples, or exposed to the air at ordinary temperatures, is somewhat remarkable, especially when the stability of the paraffin used is considered. Wraps were suspended by means of drawing-pins to wooden rods, and, after exposure to the air, were found to contain the following quantities of oil after the periods mentioned :

Original wraps Per Cent.	After 3 weeks' exposure Per Cent.	After 10 weeks' exposure Per Cent.	After 18 weeks' exposure Per Cent.
12·90	12·78	—	11·28
11·66	11·27	10·28	8·58
13·60	11·92	10·72	9·93

Oiled wraps may, therefore, lose considerably more than 3 per cent. of oil through exposure to air for a period of four months.

I have also examined oiled wraps actually used in the storage of apples in a "gas" store, and, from the results obtained, I have no doubt that considerable losses of oil occur. Therefore, the amount of oil found in used wraps must not necessarily be taken as representing the oil present in the original wraps.

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THE DETERMINATION OF ACTIVE CHLORINE

In a well-known work on the examination of water it is suggested that if the starch iodide test is positive with a water slightly acidified, active chlorine may be sought for by means of the ortho-tolidine reagent, a yellow colour indicating its presence.

It must not be overlooked that a yellow colour is also produced by nitrite and ortho-tolidine, and by nitrite and benzidine. This appears to be due to the partial hydrolysis of the diazonium salt in dilute solution, a hydroxy compound being produced which couples with the undissociated diazonium salt. This takes place feebly in acid solution, but, if the solution is made alkaline with soda or ammonia, the colour is greatly intensified.

We find that nitrite and active chlorine, in amounts usually present, may be distinguished by the fact that the starch iodide test does not give a positive result with nitrites in solutions less acid than *p*H 4, whilst active chlorine will produce a coloration in water with a reaction of *p*H 9.

Perhaps a more reliable method to follow is to test the water with *m*-phenylenediamine hydrochloride; if nitrites are present, active chlorine must be absent, since the two do not exist together. If nitrites are absent, the ortho-tolidine reagent may be used to determine active chlorine.

It may be noted that a distinct pink coloration is produced with *m*-phenylenediamine and active chlorine in concentrations exceeding 0·2 part per million.

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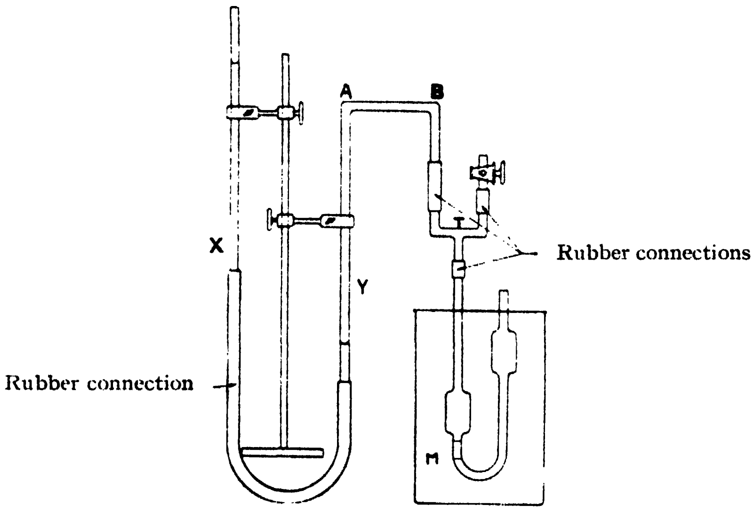
FILLING DEVICE FOR UPWARD-FLOW VISCOMETERS

The difficulty commonly experienced in filling upward-flow viscometers may be overcome simply and effectively by means of the apparatus shown in the diagram.

Y is a glass tube, bent at right angles at A, and again at B, and connected by a length of rubber tubing with a straight glass tube, X, which is supported by an adjustable clamp. Y also communicates with a T-piece (T), one limb of which is connected with the viscometer, and the other closed by a glass tap (or pinch-cock).



The liquid under examination is poured into the viscometer through the open limb (a drawn-out glass tube may conveniently be used for this purpose), and the liquid at M is controlled by adjusting the height of water (or other suitable liquid) in XY. Final adjustment is made when the liquid in the viscometer has attained the required temperature. This having been done, the glass tap (or pinch-cock) is opened, and the time of flow is noted in the usual manner.

This simple levelling device enables the final adjustment of the level of liquid in the viscometer to be made rapidly, and with a high degree of accuracy. It also eliminates the risk of fouling the walls of the viscometer above the lower reference mark (M).

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Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

BRITISH SHERRY AND THE PHARMACOPOEIA

On April 6th, an appeal was heard in the King's Bench Division (The Lord Chief Justice, Mr. Justice Avory and Mr. Justice Hawke) against the decision of Mr. Barrington Ward, who had dismissed a case against a grocer, for selling British sherry containing only 14·44 per cent. of ethyl hydroxide.

Mr. Roland Burrows, K.C., for the sampling officer, said that sherry ought to contain at least 16 per cent. of ethyl hydroxide by volume, as prescribed by the British Pharmacopoeia. The magistrate, however, had held that the Pharmacopoeia standard was applicable only to sherry intended for pharmaceutical purposes, and that it had not been proved that the purchaser had been prejudiced, since the wrapper on the bottle was transparent, and anyone could see that what was sold was British sherry, and that the analyst's certificate was not conclusive. Counsel submitted that the analyst's certificate was conclusive, and that what was sold was so deficient in one of the essentials of sherry that it could not be described as sherry.

The Lord Chief Justice said that no evidence was adduced to prove the nature, quality or substance of sherry in any sense other than that mentioned by the analyst. There was a case, relating to coffee and chicory, where the seller was held to be protected because the package described what was sold as a mixture of coffee and chicory, although that was only seen when the brown paper, in which it was wrapped up with other things, was taken off. But that did not apply to this case. The sherry was not sold as a mixture or labelled as a mixture. The bottle was labelled as British sherry. But the complaint was not that the sherry in the bottle, if there was any, was mixed with something else. The complaint was that the contents of the bottle were lacking in something essential to sherry. Here the utmost that could be said on behalf of the seller was that the label would have informed the purchaser, if he had seen it, that what he was getting was British sherry. But it was found, as a fact, that the purchaser did not see the label, though he might have done so. In these circumstances the magistrate ought to have convicted.

The other Justices agreed.

WHOLESALER'S SAMPLE

Twynham *v.* Badcock

On April 4th, the King's Bench Divisional Court, consisting of the Lord Chief Justice and Justices Avory and Hawke, allowed the appeal of an inspector under the Food and Drugs Act against the refusal of a magistrate to convict a wholesale dealer for selling ground ginger containing a preservative. The retailer of the ginger had been convicted, and proceedings were then taken against the wholesaler, but the magistrate had held that it was essential that there should be a fresh sample purchased from the wholesaler, and the sample divided and analysed.

Mr. Fox Andrewes, K.C., for the respondent, contended not only that a second sample was essential, but that there was no evidence on which the magistrate could find that his client wilfully sold the ginger knowing it to be adulterated. He relied on the invoice description.

The Lord Chief Justice, giving judgment, said that the allegation against the wholesaler was that he wilfully disobeyed the Act, because he took no steps to see that the ginger was free from preservative, but relied on the invoice description received from a vendor, who had had no analysis made for four years. It was impossible to say that there was no evidence on which the magistrate could find that the wholesaler was guilty of wilful neglect. The magistrate had refused to convict, because he thought that before there could be a conviction the same process of taking samples and having them analysed must be repeated. For this there was no warrant. The appeal would be allowed, and the case remitted to the magistrate, with a direction to convict.

The other Justices concurred.

New Zealand

SIXTY-FOURTH ANNUAL REPORT OF THE DOMINION LABORATORY

The Annual Report of the Dominion Analyst (Mr. W. Donovan, M.Sc., F.I.C.) for 1930 deals with the chemical analyses and investigations carried out on behalf of Government Departments. Of the 5541 samples examined, 3495 were received from the Health Department, and included 2486 samples of milk and 285 of human milk.

Milk.—The reductase test again proved its value for the detection of stale and insufficiently cooled milk. To comply with the Regulations, the milk must not completely decolorise the methylene blue in less than three hours. The Regulations also require that the test be applied within four hours of the procuring of the sample, and then only if the milk has been continuously kept in an ice-box from that time until the application of the test. Inspectors in the cities are provided with suitable ice-boxes.

The freezing-point test has been in constant use, and in no case has the freezing-point of genuine milk been found to vary appreciably from —0·55° C.

Iodised Salt.—Analyses of iodised salt were interesting. The standard in New Zealand is one part of potassium or sodium iodide to every 250 thousand parts of salt. Eight samples, examined in Dunedin, varied from one-third to two-and-a-half parts in 250 thousand. The iodide appeared to be unevenly distributed in the samples. In Wellington, one shipment was found to give irregular results, and five separate bags were examined. The middle portion of the salt in each bag had hardened, and portions from the surface and from the centre of the hardened salt were analysed. The results were:

Sodium iodide, parts per 250,000

	(1)	(2)	(3)	(4)	(5)
Surface ..	1·5	0·8	0·7	nil	0·3
Centre ..	3·2	1·1	1·2	nil	0·6

It will be seen that the iodide content was irregular, not only in the different bags of the shipment, but also in different portions of the same bag.

Liquors.—Under the Licensing Act it is an offence for a bottle which has contained liquor to be used again for liquor for sale, unless the label be destroyed. If re-bottling is suspected, a comparison is made with a genuine sample of the same brand, and, in the case of whisky, of the same vatting. Each distillery company furnishes a certificate that bottles bearing the same vat number have been filled with the same vatting. Determination of secondary constituents is sufficient to establish identity or difference, as the following example shows. The results are expressed in grm. per 100 litres of absolute alcohol:

	Suspected sample	Hennessey's Three Star Brandy
Fixed acidity	14·1	30·6
Volatile acidity	22·8	37·3
Compound ethers	39·3	80·1
Furfural	0·9	3·0
Extract (grms. per 100 c.c. of liquor) ..	0·86	0·57

The sample was evidently not genuine Three Star Brandy.

Soda Water.—Of 18 samples of soda water examined, drawn from soda fountains, 13 contained appreciable amounts of lead, ranging from 1/20 to 1/3 grain per gallon. The lead was derived, in some cases, from lead piping, and in others from solder used in joints. Two samples contained iron (1/5 and 2/5 grain per gallon, respectively).

Incidence of Goitre.—In the bulletin, "Goitre in School Children," by R. A. Shore and R. L. Andrew, published jointly by the Departments of Health and of Scientific and Industrial Research, the broad fact was established that where the iodine content of the soil was high, the incidence of goitre was low. In one district, however, both the iodine content of the soil and the incidence of goitre were low. Further work is being done on the iodine content of milk, eggs and vegetables from this district (also of human urine) in an attempt to solve the problem presented. The process for the determination of iodine in such material has also been investigated.

Siam

FIFTH REPORT OF THE GOVERNMENT LABORATORY

(From April 1st, 1928, to March 31, 1930)

In his Report to the Ministry of Commerce and Communications, the Director of the Government Laboratory (Mr. A. Marcan, F.I.C.) states that the official work is tending to settle down on more definite lines, owing to the enactment of the Skimmed Milk Act and the Tariff Amendment Act, and to the more regular demands of the various Departments. The total number of samples examined was 6576, and various vegetable materials were also investigated.

The Skimmed Milk Act, B.E. 2470.—In August, 1928, standards under this Act were published by the Department of Public Health, to come into force in February, 1929. The object of the Act was to prevent the importation of skimmed milk, which was being consumed in large quantities, with disastrous results to infants. The minimum standards are as follows:

Sterilised milk:	Fat,	3·25;	total milk solids,	11·75	per cent.
Evaporated milk:	,,	3·78;	,, ,, ,,	25·5	,, ,,
Condensed milk:	,,	8·0;	,, ,, ,,	28·0	,, ,,

Of the 127 samples of milk submitted, 28 were found to be below the standards. The methods of analysis adopted were those of the Milk Products Sub-Committee of the Standing Committee on Uniformity of Analytical Methods (ANALYST, 1927, **52**, 402).

DRUGS FOR THE TREATMENT OF LEPROSY.—The following analytical values were obtained for the supplies of ***Hydnocarpus anthelmintica*** oil purchased, and the mixed ethyl esters produced therefrom:

	Acidity, per cent.	Sp.gr. at 30°/4° C.	Saponification value	Iodine value (Wijs)	Specific rotation $[\alpha]^{30}_{D}$	n^{30}_{D}
Oil ..	1·0–1·9	0·945–0·949	201·7–204·3	87·0–88·2	50·4–51·1	1·4740–1·4753
Esters	0·1–0·3	0·895–0·898	189·8–194·5	80·5–82·8	42·5–44·7	1·4531

Hydnocarpus ilicifolia Oil.—Three specimens gave the following results:

Acidity (as oleic acid) per cent.	Sp.gr. at 30°/4° C.	Saponification value	Iodine value (Wijs)	Specific rotation $[\alpha]^{30}_{D}$	n^{30}_{D}	M.pt. °C.
0·6	0·947	213·1	89·7	51·2	1·4763	23–28·2
21·0	0·944	203·6	89·7	52·7	1·4739	25·8–32·6
—	0·946	202·3	89·1	51·9	1·4749	—

Clinical trials with the sodium salts and esters of these oils were made, but, so far, the results have been indecisive.

MAHWENG.—The berries of this plant, *Solanum sanitwongsei*, have a local reputation as a remedy for diabetes. An investigation was made by the British Drug Houses, Ltd., but with entirely negative results. The fruit was found to contain no alkaloid, glucoside or guanidine derivative, and large doses of an extract administered to rabbits produced no change in the blood sugar. It was suggested that its reputation might be due to some relief in the subjective symptoms, but medical evidence is lacking, and it is apparent that the matter is not worth pursuing.

TOXICOLOGICAL EXAMINATIONS.—Of 77 exhibits examined, 25 were found to contain poisonous principles, *viz.* arsenic in 15, atropine in 5, croton seeds in water 1, and mercuric oxide, mercury, gelsemium alkaloid, and poisonous insects, 1 exhibit each.

Gelsemium alkaloid.—In this case the victim was supposed to have committed suicide by taking Chinese medicinal herbs, many of which are imported into Siam, but the vegetable material submitted did not match the herbarium specimen of *Gelsemium elegans.* In a Hong Kong case (ANALYST, 1930, **55**, 754) the alkaloid gelsemidine was isolated from the stomach contents of a young Chinese woman who had committed suicide.

Poisonous Insects.—Poisonous insects are newcomers in toxicological cases. The insects, known as maleng tao ba, were used in the preparation of a drug, and administered to a child of three for the cure of a rash, with fatal result. The insects were identified as a species of *Mylabris* of the *Cantharidae* family, no doubt containing cantharidin. They were stated to have come from China.

Poisoning by "Pak Wan."—Numerous cases of poisoning by "pak wan," the leaves of *Melientha suavis*, have been submitted, and attention is drawn to the matter in the hope that other laboratories have data or theories which might help to elucidate the problem. *Melientha suavis* (*Opiliaceae*) is a small tree, of fairly frequent occurrence, and the young leaf shoots are gathered and boiled and eaten as a vegetable. It is quite a common and popular dish, but it has the unexpected property of being poisonous at times. From the exhibits received, there is no doubt that the leaves are "pak wan," and that no other tree has been mistaken for it. The usual symptoms are: giddiness and faintness, vomiting, collapse, and frequently death. Should the patient recover, a sore mouth is generally reported. From evidence collected it appears that the shoots of an individual tree may be consumed without ill results for years, but the time may come when they produce fatal results. No indication of the cause was apparent until it was observed that in a case in which death ensued, the tree from which the leaves were gathered had a number of abnormal shoots, and that many of these were infected by a small borer. It was not possible to identify this borer, but it was thought to be the larva of a moth. The evidence does not necessarily imply that the larvae are the cause of death, but the few observations which have been made do not lead to any other theory.

ANALYSES UNDER THE HARMFUL HABIT-FORMING DRUGS LAW.—Of 210 samples examined, 91 were found to contain active principles within the scope of the law. The presence of opium alkaloids in two drugs purporting to be cures for the opium habit is of interest.

The Relation Between Durability and Chemical Composition of Wood

COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH, AUSTRALIA*

THE comparatively early work on this subject (see Hawley and Wise, *The Chemistry of Wood*, New York, 1926) has indicated a relationship between the relatively few durable varieties of wood and their chemical compositions. In particular, it has been shown by Schmitz (*Idaho Forester*, 1922, p. 6), Hawley, Fleck and Richards (*J. Ind. Eng. Chem.*, 1924, **16**, 699), and by Sowder (*id.*, 1929, **21**, 981) that the relative resistance to destructive fungi may be determined in the laboratory from the toxicity of isolated aqueous extracts. This, however, is not in itself sufficient, since, for example, a certain constituent of an extract may be toxic to fungi, but not to termites (white ants) and *vice-versa*. A knowledge of the nature and specific function, if any, of each constituent of an extract is, therefore, of practical importance in connection with the preservation of timber.

In Australia, Baker and Smith (*A Research on the Pines of Australia*, Sydney, 1910; see also Cummins, Dadswell and Hill, *J. Council Sci. and Ind. Research, Australia*, 1930, **3**, 138) have examined the volatile oils from the various members of the cypress pine genus (*Callitris* spp.), the most durable, though rare, Australian wood. They obtained a crystalline and liquid fraction, *viz.* guajol and the so-called callitrol, respectively, and the latter was assumed, though on insufficient experimental evidence, to be toxic to termites. On the other hand, Oshima (*Proc. Pan-Pacific Science Congress, Australia*, 1923, p. 332) attributed the preservative power of oil from a Queensland cypress pine to the guajol, and found that high boiling-point fractions of camphor oil, which contained similar sesquiterpene alcohols, could be used successfully (and presumably economically) as preservatives.

In view of this conflicting evidence, and the scantiness of the information as to the nature of the extractives obtained with water and alcohol, I. W. and H. E. Dadswell carried out further tests on the relation between the durability and extractives of the cypress pines. Coarse sawdust or thin shavings from blocks, slabs or logs of (so far as possible) the truewoods (*i.e.* the wood between the sapwood and the pith or heart) of *C. glauca, calcarata* and *intratropica* was treated as follows:—(1) Steam-distillation and extraction of the oil from the distillate by means of ether. (2) Extraction with 96 per cent. alcohol for 6 hours in a Soxhlet apparatus, the alcohol being then removed by evaporation, and the volatile oils separated as in (1).

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* Division of Forest Products. Reprint No. 4. By I. W. and H. E. Dadswell, Nov., 1931.

In both cases phenols and acids were removed from the ethereal solution by extraction with 10 per cent. sodium hydroxide solution, guajol (white crystals, m.pt. 90° C., after recrystallisation from alcohol) being obtained as an insoluble residue. The sweet-smelling oils obtained from the alkaline mixture, before and after acidification, were then extracted with ether, and distilled under reduced pressure, the most important fraction in each case having the b.pt. 245° C. at 715 mm., and sp.gr. (15/15° C.) 0·9783. This fraction is probably the so-called callitrol of Baker and Smith, but, since uncompleted investigations by V. M. Trikojus indicate that it is an acid, the term *callitric acid* is proposed. Other fractions obtained were a liquid acid (b.pt. 150–156° C. at 18 mm.), and a viscous non-volatile oil (b.pt. 180–193° C. at 57 mm., *vide infra*).

(2*a*) Distillation of the ether-soluble portion of the semi-solid residue remaining after the removal of the volatile oils in process (2) yielded a dark green-blue oil (b.pt. 180–193° C. at 57 mm.), which set to a hard resinous mass. The insoluble portion, which, however, was slightly soluble in alcohol, was inorganic in character, and probably contained the manganese compounds which Baker and Smith (*loc. cit.*) record as characteristic of this genus.

(3) Extraction of 300 grms. of coarse sawdust for 3 hours with 3 litres of boiling distilled water, the filtered extract being concentrated to 200 c.c.

(4) Extraction by a similar procedure for 48 hours at 20° C.

YIELDS.—In general, samples of *C. glauca* and *calcarata* from New South Wales and Queensland, gave similar yields, whilst *C. intratropica* from Northern Territory (which was probably similar to that used by Oshima) contained almost twice as much material soluble in alcohol, and large amounts of volatile material containing guajol (for mean percentage yields, see Table).

Constituent (percentage yields)	*C. glauca*		*C. calcarata*		*C. intratropica*	
	Wood	Vol. oil	Wood	Vol. oil	Wood	Vol. oil
Steam distillation:						
Guajol	0·2	9·7	0·2	14·2	3·9	87
Sweet oil	0·5	21·5	0·5	30·7	—	—
Acids	1·2	50	0·8	55	0·6	15
Alcohol extract:						
Vol. in steam	2·3	—	1·4	—	4·0	—
Guajol	0·3	9·5	0·1	11·0	1·6	46
Sweet oil	0·6	17·1	0·5	40	1·7	42
Acids	1·8	54	0·6	46	0·5	12·3
Non-volatile in steam:	4·5	—	3·5	—	—	—
Ether-sol. resin in wood	3·8		2·4		—	
Do. in total extractives	56		50		—	
Ether-insol. resin in wood	0·7		1·1		—	
Do. in total extractives	9·7		22·1		—	
Soluble in alcohol	10·4		8·3		19·3	
Soluble in hot water	7·6		5·6		—	
Soluble in cold water	5·5		5·1		—	

Lower yields of volatile oils were obtained from sawdust that had been exposed.

TOXICITY TESTS.—(1) *Fomes annosus.*—Known dilutions of each constituent, diluted with sterile agar, were added to a culture medium containing 15 grms. of Merck's agar and 25 grms. of Saunders' malt extract in 1 litre of water, four 10 c.c. slopes being inoculated with mycelial flecks of this wood-destroying fungus, whilst uninoculated tubes and 4 inoculated tubes containing medium alone were used as controls; incubation was at 25–27° C. The tubes containing volatile oil were covered with waxed paper, placed over the plug, and in cases where no growth occurred during 4 weeks, the fungus was transferred to fresh medium to ascertain whether it had been killed.

Guajol had little effect on the growth of the fungus, and 1 per cent. of the sweet (*i.e.* unfractionated) oil had a retarding effect of 94 per cent., whilst 0·015 per cent. of the acids was toxic to the fungus; the resins had no effect, and were, in fact, "insoluble in the medium." A culture from a sample of rotten *C. glauca* gave similar results. Similar experiments with the aqueous extracts on the lines suggested by Hawley, Fleck and Richards (*loc. cit.*), showed retardations of 100 per cent. and 90 per cent., respectively, for 50 and 10 per cent. hot extracts of *C. glauca* or *calcarata*, and of 100 per cent. for both of the cold 50 per cent. extracts, but of only 50 per cent. for cold 10 per cent. extracts of *C. glauca.*

(2) *Termites.*—Sticks of *Pinus radiata* (4×1×0·25 inches) were dried at 105° C. for 2 hours, and immersed in solutions of the above constituents. The increase in weight, after slow evaporation at 20° C., was determined, and sticks immersed in alcohol alone served as controls. Field experiments, in which the sticks were placed in mounds of *Eutermes exitiosus* for a year, were unsuccessful, owing to the abundance of other food-material for the termites, and the effect on laboratory colonies made up of termite nest-material in stoppered glass jars was, therefore, tested. After 42 days there were signs of attack in wood treated with solutions containing 0·3 per cent. of guajol, 0·3 per cent. of sweet oil, 0·23 per cent. of non-volatile viscous oil or a saturated solution of ether-insoluble resin, and, after 192 days (during which the colonies were renewed 6 times), sticks treated with 1·4 per cent. of volatile acid and 1·9 per cent. of ether-soluble resin also showed signs of attack. It was not determined whether the dwindling of the colonies was due to natural causes or to the added materials. In view of the toxicity of the resin to termites, it is noteworthy that the wood of cypress pines contains no resin ducts and little wound tissue, the extraneous material responsible for their durability being located in the medullary ray cells and parenchyma.

These investigations suggest the possibility of treating wood with an appropriate preservative, which might be extracted from sawmill-waste or, possibly, synthesised. Future developments along these lines will, no doubt, be governed by economic considerations. J. G.

International Atomic Weights

SECOND REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS OF THE INTERNATIONAL UNION OF CHEMISTRY*

THE report covers investigations communicated to the Committee from February to October, 1931. The determination of the density of carbon dioxide at five different temperatures led to the value C=12·0054; similar measurements for sulphur dioxide gave S=32·059; and for methyl fluoride a figure nearer 19·01 than 19·00 for the atomic weight of fluorine. Comparison of the weights of specially purified krypton and oxygen by means of a micro-balance gave Kr=83·71; xenon was treated by the same method, and the higher value found by Aston (131·27) was confirmed (Xe=131·26 ± 0·005). The atomic weight of nitrogen was re-determined by means of the ratio $Ag:NH_3$, which, referred to the ratio $Ag:NO_3$ (very accurately known), allows of a calculation of $NO_3:NH_3$. The mean of eight of the most satisfactory determinations is $N=14{\cdot}0078$ ($Ag=107{\cdot}879$). The data of Hönigschmid on chlorine, now corrected for the solubility of silver chloride (0·0005 grm. per litre at 0° C.), lead to $Cl=35{\cdot}456^3$. Baxter, repeating the analysis of iodine pentoxide by thermal decomposition, found $I=126{\cdot}905$, while Hönigschmid and Striebel arrive at 126·917 by determination of the ratio $AgI:AgCl$. The atomic weights of a number of elements, calculated by Aston on the basis of mass spectrographs, are included in the report. With regard to the discovery of isotopes of oxygen, the Committee fully agrees with Aston in not considering it advisable to depart from the present chemical basis $O=16$ for atomic weights, and for more refined physical measurements, also, the weight of the atom of oxygen 16 would be advisable. The changes introduced in the Atomic Weight Table for 1932 are:

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* By G. P. Baxter, Mme. P. Curie, P. Lebeau, O. Hönigschmid, and R. J. Meyer (*Ann. Chim. anal.*, 1932, **14**, 97–107).

$Kr = 83{\cdot}7$ (older value 82·9)
$Xe = 131{\cdot}3$ („ „ 130·2).

W. R. S.

Sale of Medicated Wines

RECOMMENDATIONS OF THE ROYAL COMMISSION*

The Majority Report recommends that it should be possible to attach conditions to off-licences for druggists in the same way as can now be done for on-licences. Published recommendations of any kind of intoxicating liquor by a medical practitioner should be made illegal unless the full name, qualification and address of the practitioner are given with, and as part of, the testimonial. The various anomalies existing in the present law governing the sale of medicated wines and spirits are pointed out, and the need for bringing the licensing and excise law into harmony for both medicated spirits and wines is emphasised. A substitution of "medicines containing spirits" for the two terms "medicated spirits" and "spirits made up in medicine" is suggested, and their sale by duly qualified chemists or medical practitioners should continue to be exempt from the requirement of a justice's licence, and a corresponding exemption should be provided in revenue law. A more limited exemption, covering only those mixtures sufficiently medicated to be unfit for any beverage purpose, would be needed in those districts where there is no druggist's shop, and where such medicines (*e.g.* ammoniated tincture of quinine) are in frequent demand.

These should be labelled with directions as to dosage. The Commission regard it as possible to differentiate between "medicines rather than wines" and "wines rather than medicines." Such wines which can pass the test should be salable without justice's or excise licence, and be labelled as to dosage. Those not passing the test should be regarded as intoxicating liquors, and it should be an offence to describe them as "medicated."

The proposals as to sale of medicines containing spirits by others than druggists demand a test of medication, which should be the same for licensing and revenue purposes, and it is suggested that it be entrusted jointly to the Secretary of State and the Board of Customs and Excise or, on its appointment, the National Commission, to draw up and revise from time to time a list of spirits or wines sufficiently medicated to be incapable of use other than as a medicine or for medicinal purposes. The regularisation of the sale of absolute alcohol by chemists in quantities not exceeding 5 ozs., or of larger quantities on a doctor's prescription, is recommended, as is the exemption of perfumery and flavouring essences from the licences required for intoxicating liquors.

D. G. H.

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* Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 4s. 6d. (*Pharm. J.*, 1932, **128**, 42, 50–51.)

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Effect of Light on the Reduction of Methylene Blue in Milk. G. A. Aikins and A. C. Fay. (*J. Agric. Res.*, 1932, **44**, 85–95.)—The potentials of cream, whole milk, and skim milk drift towards the negative side when the liquids are exposed to sunlight. Potential changes, both to more positive and to more negative values, are deterred by the presence of fat, this influence being especially marked when the liquids are placed alternately in the sunlight and in the dark. Addition of fat to skim milk hastens the reduction of methylene blue in samples exposed to sunlight. Sodium oleate or stearate also shortens the time of the reduction, but, in this case, the cause is a more rapid fall of potential. The addition of methylene blue to skim milk or cream accentuates the changes in potential induced by sunlight. Various observations made confirm Whitehead's conclusion that reduction of methylene blue by light is a reaction distinct from that induced by bacteria (ANALYST, 1930, **55**, 594).

As the solution develops a progressively more negative potential, the methylene blue is decolorised whenever such potential passes through the zone of reduction characteristic of this dye. Similarly, the blue colour re-appears when the solution develops a potential sufficiently positive to oxidise the dye present. When skim milk, containing methylene blue which has been reduced by sunlight, is placed in the dark, the potential quickly becomes positive enough to re-oxidise the dye. Artificial light (electric) appreciably hastens the reduction of methylene blue in commercial milk.
T. H. P.

Phosphorus Content of Casein. R. E. L. Berggren. (*J. Biol. Chem.*, 1932, **95**, 451–460.)—The amount of phosphorus in casein has been a matter of some dispute, and it was, therefore, decided to make a further study of this subject. An attempt was first made to determine whether the amount of phosphorus in the casein is influenced by the quantity of phosphate in the milk from which it is prepared. Caseins were prepared in different ways from four portions of cow's milk. Their phosphorus contents were determined by the Fiske–Subbarow colorimetric method, and nitrogen by the Kjeldahl method. The two caseins which had been precipitated in the presence of a large excess of phosphates, had higher ratios of phosphorus to nitrogen than did the two caseins which had been prepared from milks the phosphate content of which had been reduced by dialysis. That this difference was not due merely to standing was shown by the fact that casein prepared from milk which had been kept in the refrigerator until it soured, had a slightly higher phosphorus to nitrogen ratio. Further study of the phosphorus content of caseins prepared from dialysed milks has shown that it is a relatively simple matter to prepare caseins of much lower phosphorus contents than have previously been reported for caseins obtained directly by acidification of milk. The rate of dialysis was very slightly increased by the use of a Simms dialyser. Chloroform and toluene were found to be superior to thymol in preserving the milk.

It was found that when milk was acidified, then dialysed, with chloroform as the antiseptic, the loss of total nitrogen on dialysis was the same as that for milk containing chloroform but no added acid, but the rate of loss of phosphorus on dialysis was much more rapid. The lowest value obtained for any casein was 0·29 per cent. of phosphorus, assuming that this casein contained practically the same amount of nitrogen as casein prepared from undialysed milk, namely, about 15·46 per cent. This casein was prepared from milk which had been preserved with chloroform and dialysed for 36 days before the casein was precipitated. It has not hitherto been possible to separate directly from milk caseins of such low phosphorus content. There is nothing to indicate that this low value is the minimum phosphorus content of casein. It is possible that the fractions of the mixture of proteins in milk, called "casein," contain different amounts of phosphorus, and lose phosphorus at different rates on dialysis of the milk, and that the phosphorus is much more loosely bound in the casein than has been previously supposed. Further work will be necessary to determine whether or not the loss of phosphorus from casein on dialysis of the milk is purely chemical in nature, or whether it is caused by the action of enzymes or of bacteria, or is brought about by some combination of these processes. P. H. P.

Determination of Phosphorus in Casein. R. E. L. Berggren. (*J. Biol. Chem.*, 1932, **95**, 461–464.)—In the course of an investigation on the phosphorus content of casein it became necessary to find a method, for the determination of phosphorus, which would require only small amounts of casein, and yet be sufficiently accurate for the work. The colorimetric method of Fiske and Subbarow (*J. Biol. Chem.*, 1925, **66**, 375; ANALYST, 1926, **51**, 205) has been found to be extremely suitable for this purpose. The results obtained agree well with those found gravimetrically. The method is much more rapid than those commonly employed, and only 10 or 15 mgrms. of casein are required for a determination. An average of the results obtained with nine different casein preparations gave 0·80 per cent. of phosphorus by the colorimetric method, and 0·805 per cent. by the gravimetric method. The method described in the "Report of the Association of Official Agricultural Chemists" (Washington, 2nd edition, 1925), in which the phosphorus is weighed in the form of magnesium pyrophosphate, was the gravimetric method used for comparison. P. H. P.

Rancidity Reactions of Fats. P. Bruère and A. Fourmont. (*Ann. Falsif.*, 1932, **25**, 94–97.)—*Reactions depending on iodides.—Bulir's reaction* consists in dissolving 1 grm. of fat in 10 c.c. of petroleum spirit, and adding 2 c.c. of a 20 per cent. solution of potassium iodide in 90 per cent. alcohol, followed by 15 c.c. of water. After shaking, starch is added, and a blue coloration indicates rancidity. *Lea's test* depends on heating an acetic acid and chloroform solution of fat with potassium iodide in an atmosphere of nitrogen, cooling, diluting with potassium iodide solution, and titrating with 0·02 *N* thiosulphate solution.

Taffel and Revis's Reaction.—A simplified method, which is recommended, is to dissolve 5 grms. of the fat in a cold mixture of 20 c.c. of acetic acid, 25 c.c. of 95 per cent. alcohol, and chloroform to make up to 100 c.c. One grm. of finely-powdered potassium iodide is added, the mixture is shaken, and, after 30 minutes' contact, with occasional shaking, 50 c.c. of water are poured in; the mixture is shaken, and the solution is titrated with 0·2 *N* sodium thiosulphate solution, with or without starch. By making many comparative tests with the Kreis reaction and the Vintilesco and Popescu reaction, it is concluded that if 1 c.c. of 0·2 *N* iodine is liberated by 1 grm. of fat, the fat may be regarded as rancid. D. G. H.

Nature of Antioxygens present in Natural Fats. I. Separation of Fatty Derivatives from "Antioxygens" by Distillation. T. P. Hilditch and J. J. Sleightholme. (*J. Soc. Chem. Ind.*, 1932, **51**, 39–44T.)—The capacity for oxygen absorption of olive, tung, and codling oils (at 100° C.), and of linseed oil at 70° C., has been examined; also that of their corresponding mixed fatty acids and methyl esters before and after distillation, and, in some cases, that of the glycerides re-synthesised from their distilled fatty acids. A modification of Thomas's hydrogenation apparatus was used (*J. Soc. Chem. Ind.*, 1920, **39**, 10T), and observations of the rate of absorption of oxygen were made at suitable intervals. An induction period preceding steady absorption was clearly marked in each of the original oils; it consisted of two periods, one of negligible absorption, and a succeeding interval during which absorption increases more or less slowly. Maximum rapidity was rarely attained before 50 c.c. of oxygen had been absorbed by 10 grms. of oil. The induction period was much reduced by saponification of the fats and liberation of the mixed acids, but was restored very slightly when the acids were esterified. Distillation of acids or esters led to a further decline in the period, and maximum rates of absorption afterwards were of much the same order for any particular oil and its corresponding mixed acids or esters, whether distilled or not. The shortest induction periods in the respective series were for glycerides prepared synthetically from the distilled acids of olive or linseed oils. Five fractions of increasing boiling point and iodine value were prepared by distilling the mixed esters of olive and linseed oils *in vacuo*, and the induction period in these series was found greatest in the fractions of low boiling point, and at a minimum in the penultimate fractions consisting almost wholly of unsaturated esters of the C_{18} acids. Results are considered to confirm the view that natural anti-oxygenic compounds accompany the original fatty oils, and cause the "induction periods" on exposure to the action of oxygen. These may not all be of the same type, and proteins or their degradation products may possess such properties. Preliminary experiments with olive oil show that the induction period is almost eliminated on boiling the oil with dilute hydrochloric acid or giving a very mild treatment with insufficient caustic alkali to effect appreciable hydrolysis. Shaking with concentrated sulphuric acid yielded an oil more resistant to the action of oxygen than the original. D. G. H.

Detection of Bilberry Juice in Red Wine. W. Diemair. (*Chem. Ztg.*, 1932, **56**, 247.)—The filtrate obtained after decolorisation of wine by heating it for a short period with charcoal, probably contains some of the original colouring matter in the form of a "colourless isomer," since the colour may be partly regenerated by the action of concentrated hydrochloric acid at the boiling point. In this way a slight yellow-red colour was obtained from red wine, whilst bilberry wine, alone or in admixture with red wine, showed a colour change through blue, green-blue and blue-violet to yellow-brown. These reactions, which are due to the presence of oenidin dimethyl ester and myrtillidin monomethyl ester, respectively, may be used to detect adulteration (*cf.* Ofner, ANALYST, 1931, **56**, 672).

J. G.

Determination of Ammonia, Trimethylamine, and other Amines in Foodstuffs. F. Okoloff. (*Z. Unters. Lebensm.*, 1932, **63**, 129–154.)—The literature on these determinations is reviewed critically, and, as the result of experiments on the distillation of amine and ammonia mixtures, and on the behaviour of the distillates towards formaldehyde and nitrous acid, the following methods of determination are proposed:—*Ammonia in the presence of Primary Amines.*—Three hundred c.c. of liquid containing an artificial mixture of ammonium sulphate with methylamine (or with herring-extract), are distilled with magnesium oxide into an excess of standard sulphuric acid, and the distillate is evaporated to 75 c.c., and, when cool, titrated with alkali until faintly red to phenolphthalein. The colour is then discharged by 1 drop of 0·1 *N* acid, and the liquid is evaporated to dryness on the water-bath, 30 c.c. of alcohol being added at the last stages. The dry residue is cooled in a desiccator, and extracted for 1 minute with one 40-c.c. and two 30-c.c. portions of 96 per cent. alcohol, the extract being filtered into one flask, whilst the solid residue is extracted with warm water, and this extract filtered into another flask. Formol titration by the usual method (*vide infra*) is then applied to both solutions (after dilution, in the former case, with 200 c.c. of cold boiled water). The amine nitrogen and ammoniacal nitrogen are obtained, respectively, from the alcoholic and water extracts with figures ranging from 102 to 105 per cent., in the presence of 4 to 9 and of 20 mgrms. (as *N*) of the respective compounds. *Trimethylamine in the presence of Methylamine and Ammonia.*—Two 300-c.c. portions of herring-extract, to one of which a known amount of trimethylamine had been added, were used. The solutions are distilled into excess of 0·1 *N* acid, and the distillate, after 15 minutes at the boiling-point, is cooled and titrated in the presence of 0·2 c.c. of a 0·2 per cent. solution of rosolic acid, in order to obtain the total volatile bases. The neutral liquid is then boiled for 40 minutes with 15 grms. of sodium nitrite and 25 grms. of glacial acetic acid, in a total volume of 300 c.c., in order to decompose any methylamine into nitrogen and methyl alcohol, and three-quarters of the volume of the resulting liquid is then distilled in the presence of 50 c.c. of 30 per cent. sodium hydroxide solution into an excess of 0·1 *N* acid. If carbon dioxide is removed from the distillate by boiling, and the excess of acid in the cool liquid is titrated in presence of rosolic acid, the factor 1·4 gives the trimethylamine nitrogen. The accuracy in the presence of 3 to 17 mgrms. of total nitrogen, and 3 to 13 mgrms. of trimethylamine nitrogen is about 95 to 104 per cent. for both compounds. *Ammoniacal Nitrogen and Amino Nitrogen in Herrings.*—The viscera and bones are removed, and 50 grms. of the minced flesh are extracted for 24 hours in the ice-chest with 1 litre of water, the mixture being then shaken well and, after 30 minutes, strained through a sieve. The extract is then divided into two 400-c.c. portions, and treated as described above, in order to obtain (*a*) the total volatile nitrogen, and (*b*) the trimethylamine nitrogen, while (*c*) the ammoniacal nitrogen is determined in one of the distillates (neutral to rosolic acid) by titration with 0·2 *N* alkali, after addition of 20 c.c. of clear formalin. The accuracy of formol titration for the determination of ammonia was shown to be affected by the presence of 5 to 10 mgrms. of a primary amine, though not by secondary amines, rosolic acid being preferable as indicator in the presence of 5 to 25 c.c. of trimethylamine (accuracy 99 to 106 per cent. for 2 to 10 mgrms. of ammoniacal nitrogen). In the absence of trimethylamine, neutral red, litmus, phenolphthalein or rosolic acid solutions have an accuracy of 97 to 101 per cent. for 1 to 50 mgrms. of ammoniacal nitrogen; methyl red is unsuitable. Tests on 39 samples of herrings showed a positive Eber's test reaction in 28 cases, and ammoniacal nitrogen, trimethylamine nitrogen, and other volatile nitrogen contents of 1 to 181, 0 to 18, and 0 to 13 mgrms. per 100 grms. of herring, respectively. J. G.

Occurrence and Detection of Choline in Coffee. F. E. Nottbohm and F. Mayer. (*Z. Unters. Lebensm.*, 1932, **63**, 176–182.)—It has been shown (*id.*, 1932, **63**, 47) that certain difficulties in the determination of trigonelline in coffee extracts are associated with extracts containing large amounts of sugars. A similar cause is now suggested as an explanation of previous failures to find choline in coffee extracts, and the autoclave method, suggested by the authors for the determination of trigonelline, has been applied to this end. The trigonelline chloride is, therefore, removed, as already described (*loc. cit.*, and ANALYST, 1931, **56**, 405, 543), and the clear filtrate is evaporated until free from alcohol, and is then diluted to 50 c.c. with hot water, after which the sugars are destroyed by the action of 10 c.c. of hydrochloric acid (sp.gr. 1·124) in an autoclave at 4·5 atmospheres. The resulting solution is warmed with animal charcoal, and then filtered and evaporated to a syrup, the cool mass being extracted with 40 c.c. of absolute alcohol. The alcohol is removed from the clear extract, and a solution of the residue, in 25 c.c. of water and 3 c.c. of hydrochloric acid, is again treated with animal charcoal, the solution being evaporated in a vacuum, and the residue then extracted 3 times with 5 c.c. of absolute alcohol. The choline is finally precipitated from a solution in 25 c.c. of water and 2 c.c. of acid, by addition of 10 to 15 c.c. of a 20 per cent. solution of phosphotungstic acid in water. It is filtered off, and washed with 5 per cent. hydrochloric acid, and is then decomposed by addition of a cold saturated solution of barium hydroxide. After removal of the barium phosphotungstate, the filtrate is acidified and evaporated at a low pressure. The residue is extracted twice with 7 c.c. of cold absolute alcohol, and the residue, after evaporation and drying over sulphuric acid, is ready for the determination of choline (*cf.* Roman, *Biochem. Z.*, 1930, **219**, 218). It is, therefore, dissolved in 10 c.c. of water, and 1 c.c. of this solution is mixed with 0·3 c.c. of a solution containing 157 grms. of iodine and 200 grms. of potassium iodide per litre. After 30 minutes at 0° C., the dark-brown needles of the choline-iodine compound are separated by filtration, and are washed with 5 c.c. of ice-water, and a solution of the residue in 10 c.c. of absolute alcohol is then titrated with 0·1 *N* sodium thiosulphate solution by the procedure described for trigonelline (*loc. cit.*); 1 c.c. ≡ 1·335 mgrms. of choline. Santos coffee (250 grms.) contained 0·022 per cent. Choline compounds:—$C_5H_{14}NOCl,AuCl_3$, golden needles or prisms, soluble in water, dilute hydrochloric acid, or alcohol, m.pt. 245 to 249° C., with decomposition; $C_8H_{14}NOCl,PtCl_4$, orange prisms or plates, soluble in water or dilute alcohol, m.pt. 233 to 234° C., with decomposition; $C_8H_{14}NOCl,6HgCl_2$, colourless hygroscopic prisms or needles, soluble in water or 96 per cent. alcohol, m.pt. 240 to 243° C. J. G.

Determination of the Saccharin Content of Foodstuffs and Beverages, and particularly of Beer. J. E. Heesterman. (*Chem. Weekblad,* **1932, 29,** 130–134.)—The present work is based on the method of Lerrigo and Williams (ANALYST, 1927, **52**, 377), though it is considered that this method is unsuitable for beer on account of the impure nature of the final residue, and of the difficulty of obtaining its ammonium content by a direct colorimetric method. Detailed investigations of the individual stages of the method resulted in the following optimum working conditions:—Normally, 50 c.c. of beer and 5 c.c. of 4 *N* hydrochloric acid are shaken with 100 c.c. of a mixture containing equal volumes of petroleum spirit (b.pt. 40 to 60° C.) and ether. The extract is evaporated until less than 50 c.c. remain, and this residue is transferred with a little solvent to a 50 c.c. flat-bottomed flask, and evaporated to dryness. The residue is heated with 10 c.c. of 3 *N* hydrochloric acid for 1½ hours under a reflux condenser (a diagram of a convenient micro-form is given), and 10 c.c. of 4 *N* potassium hydroxide solution are then added to the cool mixture. The ammonia is removed by distillation, at the rate of about 3 c.c. in 5 minutes, through a tube, bent so as to avoid contamination of the distillate by priming, into a test-tube cooled in water. In this way most of the ammonia is obtained in the first few c.c., and may be titrated with 0·001 *N* hydrochloric acid in the presence of 2 drops of a 0·02 per cent. solution of methyl red (previously adjusted, by addition of 0·1 *N* hydrochloric acid, until red in colour). The resulting solution is then diluted until about 0·00005 *N* to ammonia, and matched by Nessler's method against a suitable standard containing ammonium sulphate. The usual precautions for obtaining ammonia-free reagents, water and apparatus are indicated, but allowance should, nevertheless, be made for any blank obtained by a repetition of the whole process without the beer. The method was tested on 21 varied samples of beer containing 0 to 200 mgrms. of the crystalline sodium derivative of saccharin ($+2H_2O$) per litre, and was found to be sensitive to 5 mgrms. per litre. A more refined process, sensitive to 1 mgrm. per litre, is also described, in which 150 c.c. of beer and 15 c.c. of acid are extracted with 300 c.c. of the solvent mixture, the extract being then shaken with 40 c.c. of *N* potassium hydroxide solution, and washed with 10 c.c. of water. The alkaline liquors, which contain all the saccharin, are acidified with 5 c.c. of hydrochloric acid (sp.gr. 1·19), and, after a further extraction with the solvent mixture, the procedure already described is followed. In general, titration gave results a few mgrms. per litre higher than the colorimetric method. J. G.

New Reactions of Salts of Quinine. Volumetric Method for Determining the Alkaloid. M. J. Papavassiliou and J. Georgiadès. (*J. Pharm. Chim.*, **1932, 124,** 167–177.)—To the known precipitants of quinine may be added palladium chloride. If to a 1 per cent. solution of palladium chloride a few drops of a neutral quinine solution are added, a yellowish amorphous precipitate, insoluble in alcohol and soluble in acids, is formed. Oxidising substances modify the precipitate. In the presence of chlorine water a flocculent yellowish precipitate forms, and as little as 0·001 grm. of quinine in solution may be detected. The precipitate, if allowed to form slowly from a hot solution, forms very small, fine, colourless crystals of characteristic form. With hydrogen peroxide the precipitated crystals are similar, but reddish. In the presence of 5 per cent. chromic acid and an equal volume of 1 per cent. palladium chloride, an amorphous bright yellow precipitate is formed, soluble in boiling water, sparingly soluble in alcohol, and insoluble in ether and chloroform, and the reaction is capable of detecting 1 part of quinine in 6000. With cinchonidine, cinchonine and quinidine similar precipitates are formed; with papaverine a microscopically distinct yellowish precipitate; with solanine a yellow powdery precipitate; and with brucine and strychnine yellow precipitates, turning reddish-brown. The strychnine precipitate is entirely crystalline, and may readily be distinguished under the microscope from that of quinine. In the presence of sulphuric acid, quinine reduces alkaline chromates and dichromates, as is the case with cinchonidine, quinidine, aconitine, pilocarpine, and colchicine. The reduction of potassium permanganate forms a convenient method of determining quinine. The quinine sulphate (0·1 grm.) is dissolved in 100 c.c. of water; 10 c.c. of (1:3) sulphuric acid are added, and the mixture is heated at 50 to 60° C., after which 50 c.c. of 0·1 *N* potassium permanganate solution are run in, the whole carefully mixed, and 0·5 grm. of oxalic acid added. The liquid is then titrated with 0·1 *N* potassium permanganate solution until a faint pink colour persists for a few seconds. After reduction, the liquid shows a characteristic fluorescence. D. G. H.

Biochemical

Assimilation of Aluminium by the Human System. S. Judd Lewis. (*Biochem. J.*, 1931, **25**, 2162–2167.)—A spectrographic method was employed for determining aluminium in blood and in milk: the material was evaporated, and the residue gently ignited until free from carbon; the ash was transferred to the lower electrode of an arc-lamp, and the spectrum observed in the usual way, by means of a large Hilger quartz spectrograph, the intensity of the two principal aluminium lines giving a measure of the aluminium present. The lines could be recognised with certainty when the concentration of aluminium was one part in 10 millions. It was found that normal blood usually contains no aluminium, and when it does contain any, the proportion is very small, 0·3 part per million being the highest value recorded. Aluminium, in amounts ranging from nil to 1·3 part per million (in one case 5 parts), was found in the blood of persons who had included a meal of scones containing 94 mgrms. of aluminium (the form in which the aluminium was present is not stated) in their normal daily diet. Aluminium was not detectable in the blood until 4 to 5 hours after the special meal; the maximum quantity found remained constant during the period over which special meals were taken. Milk (human, cow's, and goat's) was found normally to contain either *nil* or, at the most, in the case of cow's milk, 0·3 part per million of aluminium; an increase of a fraction of one part per million in the aluminium content was detected in most of the samples taken several hours after the subject had been given a dose of alum. S. G. C.

Determination of Sugars in Plant Extracts. T. G. Phillips. (*J. Biol. Chem.*, 1932, **95**, 735–742.)—In order to be able to make a satisfactory choice among the methods available for the determination of sugars in plant extracts, and to make the best possible interpretation of the results obtained, it seemed necessary to study the following points:—(1) The comparative action of a number of oxidising reagents on a variety of plant materials. (2) The behaviour of these reagents toward sucrose hydrolysed by invertase. (3) The most reliable method for the calculation of sucrose hydrolysed by invertase when determined in the presence of reducing sugars. The results obtained by the use of four oxidising solutions, including three differing degrees of alkalinity, are now reported. The solutions are Fehling's solution, the micro-reagent of Shaffer and Hartmann (*J. Biol. Chem.*, 1920, **45**, 365), Tompsett's reagent (*Biochem. J.*, 1930, **24**, 1148) and a bicarbonate solution. It is shown that no one of the four oxidising reagents is best for all the plant extracts used. It is probably safe to assume that the reagent giving the lowest amount of sugar in a given extract has determined all the true sugars present, and that the excessive values obtained by the other methods are due to non-sugars to which these reagents are sensitive. So far as the materials studied are indicative, it appears that a choice may be made by comparing Fehling's solution and the bicarbonate reagent. Comparison with the Shaffer–Hartmann reagent is suggested, as, because of its convenience, it is preferred for use with extracts to which it can be applied. As used in the study, Fehling's solution is not reliable for the determination of amounts of glucose less than 5 mgrms. It may be used to determine as little as 2 mgrms. of sucrose in the presence of 5 mgrms. or more of glucose. The calculations of sucrose determined in the presence of reducing sugars must be made in a manner suited to the peculiarities of the oxidising reagent used. P. H. P.

New Colour Test for Cysteine. E. Dyer and O. Baudisch. (*J. Biol. Chem.*, 1932, **95**, 483–489.)—The highly distinctive naphthoquinone test for cysteine, important for the detection and determination of sulphur-containing amino acids, requires the presence of three free groups in the molecule, namely, $-SH$, $-NH_2$ and $-COOH$, a fact which partly explains its remarkable specificity. A similar unusual degree of specificity has now been observed in the reaction of *o*-benzoquinone with cysteine. When an aqueous solution of cysteine hydrochloride is shaken with a chloroform solution of *o*-benzoquinone a deep red colour is produced in the chloroform layer. The test appears to be a specific qualitative reaction for cysteine; the chemistry of the colour reaction has not yet been studied in detail. To prepare the *o*-benzoquinone a mixture of 0·4 grm. of catechol, 1·5 grm. of anhydrous sodium sulphate, 1·5 grm. of silver oxide, and 10 c.c. of dry ether was shaken in a test-tube for 35 seconds, then filtered at once. The ethereal filtrate, chilled in a freezing mixture, deposited red crystals of the quinone, which were separated by decantation, washed once with 1 to 2 c.c. of ether, and dissolved in 8 c.c. of chloroform. Two c.c. of the freshly-prepared solution were used for each test. When 2 c.c. of an aqueous solution of cysteine hydrochloride which contained 0·001 grm. of cysteine per c.c., were added to 2 c.c. of the chloroform solution of the quinone, and the mixture shaken vigorously, the pleochromatic colour of the chloroform layer was first discharged, giving a pale yellow. On further shaking for about 2 minutes a deep red colour was developed in the chloroform layer. The aqueous layer gradually became pink on prolonged standing, owing to decomposition of the quinone itself. The test was always made in a neutral or weakly acid medium. The red cysteine-quinone-chloroform mixture is immediately decolorised by reducing agents, such as sodium sulphite solution, sodium cyanide solution, or hydrogen sulphide, and is slowly decolorised when shaken with an oxidising agent, such as perhydrol. Cysteine cannot be detected by the *o*-quinone test in concentrations smaller than 10 parts per million. With high concentrations of cysteine a large excess of quinone is necessary for production of the characteristic colour. No other amino acids and sulphur-containing compounds so far investigated have given the colour, and it is shown that the reaction may be used to detect cysteine in the presence of cystine, glutathione, and many other sulphur and nitrogen compounds. The sensitivity of the test is lessened by the presence of relatively large quantities of glutathione, but is unaltered by the presence or absence of alanine. The effect of various solvents for the *o*-quinone was tried, but chloroform was found to be most suitable. It is shown that the test is also applicable to cystine by reduction to cysteine; the limit of sensitivity of this test is 100 parts of cystine per million. P. H. P.

Serum Diagnosis in the Investigation of Foodstuffs. C. Griebel and H. Maass. (*Z. Unters. Lebensm.*, 1932, **63**, 166–176.)—Uhlenhut's precipitin test may be applied to the detection of extracts of certain seeds which are not easily distinguishable by microscopic or chemical methods. The procedure is to remove the fat from the finely-ground seeds by extraction with ether, the sugars and free plant-acids then being extracted with 70 per cent. alcohol, and the residue dried in a desiccator. It is next extracted with physiological salt solution at room temperature or in the incubator, and 2 to 5 c.c. of the filtered liquid are injected 6 to 12 times into the auricular veins of dogs at intervals of 2 to 4 days. The serum is then withdrawn and tested in dilutions of 1:200 to 1:3,000 by the usual Uhlenhut method, observations being made in all cases after 20 minutes; 0·1 c.c. of normal dog-serum +1 c.c. of antigen, and 0·1 c.c. of antiserum + 1 c.c. of physiological salt solution should be used as controls. Sera obtained from extracts of both almond and apricot stones reacted towards both of these, but were not sufficiently specific to distinguish these stones from one another; attempts to distinguish the resulting precipitates by fractional precipitation, or by other methods, also failed. The serum from walnuts did not give a reliable specific reaction for this seed, but specific sera were obtained from pine seeds and from cashew (anacardium), hazel nuts and arachis nuts. It was possible in this way to detect small amounts of these nuts when present as foreign ingredients in marzipan or persipan; almonds, hazels, arachis nuts, and walnuts, were also detectable in chocolate. An anti-serum prepared from plasmon, and diluted to 1:2,000, was used to detect 1 per cent. or more of plasmon in the binding substance of sausages. J. G.

Preparation of Crystallised Anti-Beri-beri Vitamin from Yeast. R. Tschesche. (*Chem. Ztg.*, 1932, **56**, 166–167.)—The known reactions of vitamin *B*1 have been confirmed, and certain new reactions ascertained. On the basis of this information, a number of methods of separating the vitamin, resulting finally in a pure product, have been developed. The procedure employed consisted mainly in adsorption of autolysed brewery yeast on fuller's earth, precipitation of foreign substances with silver nitrate, mercuric sulphate and lead acetate, and application of Seidell's benzoylation process. In this way 100 c.c. of extract, corresponding with 50 kilos. of yeast, were obtained. Treatment of this extract, with gold chloride or picrolonic acid gave an amorphous precipitate, and when this was filtered off, the filtrate yielded crystals of the vitamin aurichloride or picrolonate within a few hours. After crystallisation of the picrolonate from water and conversion into the hydrochloride, 70–80 mgrms. of crystalline product were obtained (from 100 kilos. of yeast). These crystals contain both nitrogen and sulphur, and the free base has the probable formula $C_{12}H_{17}ON_3S$. By its sulphur content, vitamin *B*1 resembles insulin and glutathione. The compound is optically inactive, and in ultra-violet light it shows an absorption maximum at 250 to 260 mμ, as was found by Guha and Damianovich for vitamin *B*1 preparations made from yeast.

The results of a large number of tests give for the pigeon-unit the value 2·4γ. The crystals are thus the most active material yet obtained, and the fact that the activity is not changed by conversion of the hydrochloride into the gold salt or picrolonate and back to the hydrochloride, indicates the material to be pure vitamin *B*1. A sample of Jansen and Donath's preparation, made from rice, and supplied by these authors, was also found to contain sulphur, so that the formula $C_6H_{10}ON_2 + HCl$ is inaccurate. The mixed melting-points of the two hydrochlorides showed no depression. The sulphur present is moderately labile, and is split off by cold potassium permanganate solution, or by concentrated nitric or sulphuric acid, and when the compound is boiled with barium hydroxide solution hydrogen sulphide is evolved. T. H. P.

Lovibond Values of the Liver-Oils of various Animals, and Growth Promotion of different Vitamin Preparations. P. Karrer, H. v. Euler and K. Schöpp. (*Helv. Chim. Acta*, 1932, **15**, 493–495.)—For the liver-oils of a number of animals, birds, and fishes, which had mostly died from disease, the Lovibond values for the reaction with antimony chloride have been determined. High values are shown for the liver-oils of various fish, *e.g.* sole (350), salmon (143), *Hippoglossus hippoglossus* (200), *Scombresox saurus* (500), turbot (800), and *Stereolepsis ischinagi* (about 3000). Among birds, the cormorant, which feeds largely or wholly on fish rich in vitamin *A*, gives the value 0; the same is the case with the seal. The liver-oil of the hen, after feeding on grass and carotene, shows the value 400–500, or, after normal feeding, 75. Of the mammals, the pure carnivora (lion, tiger) give zero values, the bear traces, and the zebra 53. Among reptiles, *Coluber quadrilineatus* shows the value 0, *Lacerta ocellata* 200, and *Basilicus americanus* 400. The amphibian, *Amblystoma*, gives the value 0.

Biological tests on a number of vitamin *A* and vitamin *A* ester preparations gave the following results, the cod-liver oil values (C.L.O.) being calculated from the formula, (20 × blue value) ÷ (mgrms. of substance per c.c.):

	C.L.O.	Daily dose	Increase in weight per day
Vitamin *A* from *Scombresox saurus*, regenerated from the *p*-nitrobenzoate	8000	$1{\cdot}2\gamma$	0·45 grm.
Vitamin *A* stearate from *Scombresox saurus*	3000	4	0·5
Vitamin *A* acetate ,, ,, ,,	7000	2	0·7
Vitamin *A* from *Hippoglossus hippoglossus*	8800	1	0·4
Vitamin *A* from the turbot	9800	0·5	0·9
,, ,, ,, ,, ,, ...	9800	0·3	0·55
After fractional adsorption on kaolin of the part of *H. hippoglossus* vitamin *A* not adsorbed by the adsorbent ..	8000	1	0·8
,, ,, ,, ,,	8000	0·5	0·5

T. H. P.

Application of the Carr-Price Reaction to Carotinoids. B. v. Euler and P. Karrer. (*Helv. Chim. Acta*, 1932, **15**, 496–502.)—The reagent used was prepared by saturating washed, dried and distilled chloroform at 20° C. with antimony chloride, which had been previously dried and washed with chloroform. Into 0·2 c.c. of the chloroform solution of the substance to be tested, 2 c.c. of an antimony chloride solution of definite concentration was run from a micro-burette, the colour being then determined in a 10 mm. layer of the liquid in a Lovibond tintometer. The measurements were made by the two authors in Stockholm and Zurich, respectively.

The results thus obtained with a number of different carotinoids vary with the time of the reaction, the mode of mixing, etc., and are apparently influenced to some extent by the conditions of illumination of the apparatus. If the blue coloration attains its maximum intensity within the first three minutes, it is suitable for use in calculating the C.L.O.-value. The accuracy of the above procedure, as applied to carotinoids, is estimated at about 10 per cent. T. H. P.

Action of Selenious Anhydride on Sterols. E. Montignie. (*Bull. Soc. Chim.*, 1932, **51**, 144.)—A red precipitate of selenium, or a red coloration, is obtained when a solution of ergosterol in 95 per cent. alcohol is boiled with 3 to 4 c.c. of aqueous selenious anhydride solution. With a few mgrms. of ergosterol in 5 c.c. of the alcohol, the reaction is detectable after 1 to 2 minutes' boiling. The minimum amount of ergosterol detectable is about 0·0006 grm. Derivatives of ergosterol, *e.g.* γ-dihydroergosterol acetate, also give the reaction, but with diminished intensity. Other sterols, such as chemically pure cholesterol, stigmasterol and the phytosterols, give negative results. Irradiation of ergosterol is accompanied by progressive diminution in the intensity of the reaction, owing to the formation of the yellow resin resulting from the destruction of the irradiated ergosterol or vitamin *D*. T. H. P.

Quantitative Determination of Alpha-dihydroergosterol in Ergosterol from Ergot. M. C. Hart and H. Emerson. (*J. Amer. Chem. Soc.*, 1932, **54**, 1077–1078.)—A typical ergosterol preparation was analysed by first fractionally separating 100 grms. into 4 crops of crystals and a final mother liquor, and finding the specific rotation of each fraction. From these values, and on the assumption that a mixture of ergosterol ($[\alpha]_D = -132°$) and α-dihydroergosterol ($[\alpha]_D = -20{\cdot}4°$), was being dealt with, the composition was calculated, and not less than 30 per cent. of α-dihydroergosterol was found. A third sterol, in minute quantity, was possibly present.

D. G. H.

Purification of Benzidine, and an Improved Reagent for Determination of Haemoglobin in Blood. F. C. Bing. (*J. Biol. Chem.*, 1932, **95**, 387-388.)—In the quantitative determination of haemoglobin, by the method of Bing and Baker (*J. Biol. Chem.*, 1931, **92**, 589), a very good grade of benzidine is essential, and many samples, including expensive products, have been found unsatisfactory, even after purification, as recommended. By means of the following method of purification, a suitable reagent was obtained from all the samples of benzidine that were tried. The method depends upon the fact that the interfering substances in most commercial specimens of benzidine are soluble in 50 per cent. alcohol, Twenty grms. of benzidine base are dissolved in 200 c.c. of ordinary ethyl alcohol, with gentle heating, and filtered to remove insoluble material. The filtrate, after the addition of 1 grm. of blood charcoal (extracted with hydrochloric acid and re-activated), is stirred, and kept at a temperature of 50° C. ± 10° C. for 15 minutes. This can best be done on an electric hot plate. While warm, it is filtered, and the charcoal is washed with 10 c.c. of warm alcohol. The treatment with charcoal is repeated until the filtrate is almost colourless. Two to three additions of charcoal are usually sufficient, but with highly coloured products ten to twelve treatments may be necessary. To the filtrate 135 c.c. of distilled water are added, or sufficient water to make the alcohol 50 to 60 per cent. by volume, and the whole is warmed, if necessary, to obtain a clear solution, and then left in the refrigerator for 24 to 48 hours to crystallise the benzidine. The crystals are dried by suction on a Buchner funnel, washed with cold 50 per cent. alcohol, dried by continued suction, and preserved in a bottle protected from light. From 20 grms. of a highly coloured technical product 12 grms. of purified material were obtained. All benzidine so prepared has given a negative result when tested as follows:—With the aid of heat, 1 grm. of purified benzidine is dissolved in 20 c.c. of glacial acetic acid, and 30 c.c. of distilled water, and 50 c.c. of ordinary 95 per cent. alcohol are added. This constitutes the reagent now used in the haemoglobin determinations. The solution may have a trace of yellow colour, but decolorisation with charcoal at this stage is not desirable. In a test tube are placed 2 c.c. of the reagent, 1 c.c. of distilled water, and 1 c.c. of 0·6 per cent. hydrogen peroxide, and mixed. No coloration, or only a very slight yellow tint, should develop in 2 hours. If this mixture is diluted to 25 c.c. with 20 per cent. acetic acid, and viewed through a thickness of about 1 cm., it should be practically indistinguishable from distilled water. The new reagent gives, with blood, exactly the same amount of colour as the old one, even though the concentration of benzidine is halved. For haemoglobin determinations the technique of Bing and Baker is followed, except that 2 hours are allowed for full colour development. The reaction mixture may, if desired, be allowed to stand for several hours before dilution to 25 c.c.

P. H. P.

Toxicological

Presence of Lead in the Herbage and Soil of Lands Adjoining Coke-Ovens and the Illness and Poisoning of Stock Fed Thereon. J. T. Dunn and H. C. L. Bloxam. (*J. Soc. Chem. Ind.*, 1932, **51**, 100–102T.)—The examination of soil and herbage in the vicinities of several coke-oven works in different districts showed that lead, manganese and copper were present in considerable proportions. The investigation was the outcome of the mysterious deaths of cattle and sheep. In the case of a sheep, the kidneys contained 1·7 part per million of lead, and 2·1 parts of copper; manganese, 0; the liver (part only), 2·6 parts of lead, 3·5 parts of copper, and no manganese; the stomach tissue, 0·6 part of lead, 3·2 parts of copper, and 8·3 parts of manganese; stomach contents, 0·2 part of lead, 1·8 part of copper, and 7·2 parts of manganese. The stomach and intestines of a dead bullock from the same farm contained 0·8 part of lead per million; 1·0 part of copper, and 97·0 parts of manganese. Soil, sub-soil (2 ft. below the surface), and grass in fields on this farm contained, respectively, in field A, lead 1·1, 0·4, 14·1; copper, 17, 3 and 4·7; manganese, 43, 158 and none; field B, soil, grass and turf near road, lead, 5·5, 11·5, 2·2; copper, 24·4, 4·2 and 26·7; manganese, 84, none and 74; field C, lead 1·1, copper 8·7, and manganese 14 parts per million, whilst for fields in other industrial districts figures were considerably higher.

Experiments so arranged as to exclude the possibility of the metals being derived from wind-blown soil or dust are now in progress, to confirm the inference that lead and copper are being introduced at the present time. Samples of soil, herbage, and grass, from purely agricultural districts, in no case contained lead or copper, and it is evident that any industrial process involving consumption of large quantities of coal might emit lead and copper compounds in sufficient quantity to poison neighbouring pastures. D. G. H.

Organic Analysis

Highly Sensitive Reagent for Hydrazines and Analogous Compounds. E. Montignie. (*Bull. Soc. Chim.*, 1932, **51**, 127.)—When heated with selenious anhydride solution (4 per cent.), hydrazine, phenylhydrazine, etc., give a red precipitate of selenium. When 5 c.c. of the reagent are used, 0·00025 grm. of phenylhydrazine, 0·0001 grm. of semicarbazide hydrochloride, or 0·001 grm. of phenylsemicarbazide is detectable in this way. Inversely, when two or three drops of phenylhydrazine are dissolved in 10 c.c. of water acidified with hydrochloric acid, and the solution is heated with selenious anhydride solution, about 0·0003 grm. of selenium is detectable by the formation of the red precipitate. (*Cf.* ANALYST, 1930, **55**, 294.) T. H. P.

New General Reagent for the Enolic Form. E. V. Zappi. (*Bull. Soc. Chim.*, 1932, **51**, 54–59.)—Compounds with free enolic modifications, that is, containing the group ·C(OH):CH· in the molecule, such as acetylacetone, ethyl acetoacetate, or ethyl malonate, reduce mercurous nitrate solution with formation of very finely divided mercury, the extent of the reaction being apparently proportional to the concentration of the enols in the solution. Compounds existing in the pseudo-forms, imino-alcohol [$\cdot C(OH){:}N\cdot$], thio-imino-alcohol [$\cdot C(SH){:}N\cdot$], isonitrile ($:C{:}NH$), iso-cyano- ($O{:}C{:}N\cdot$) and isothiocyano-compounds, and isonitro-compounds [$:C{:}N(OH){:}O$], effect similar reduction. The same is the case with compounds containing active unsaturated linkings of the allyl ($R\cdot CH_2\cdot CH{:}CH\cdot$ or $R\cdot CH_2\cdot CH{:}CHR$) or acetylene type ($CHR\vdots CHR$). Theobromine, with enolic structure, responds to this reaction, whereas caffeine, in which the only labile hydrogen is replaced by a methyl group, does not react. Camphor, which contains in its molecule the enolisable group $\cdot CO\cdot CH_2\cdot$, also gives a negative result, but it has been found that the enolic structure is assumed only when the camphor is dissolved in sodium ethoxide, or is in presence of Grignard reagent. As a test for enolic compounds, mercurous nitrate is far more satisfactory than ferric chloride, which is by no means specific.

The reagent is prepared by treating 50 grms. of mercury with 50 grms. of nitric acid (sp.gr. 1·2) in a porcelain dish, separating the resulting crystals after the lapse of 24 hours, and dissolving them in 5 parts of boiled distilled water containing 10 per cent. of nitric acid. It is stored in presence of a small amount of mercury.

The compound to be tested is dissolved in 4 to 5 times its volume of alcohol, and the solution then treated with its own volume of the reagent. With much free enolic modification, the grey precipitate of mercury forms immediately; otherwise the liquid requires short boiling (usually less than 30 seconds). If necessary, other solvents without action on mercurous nitrate, such as water, ethyl or amyl esters, petroleum spirit, glycerol, or chloroform, may be used, miscibility of the solvent with the aqueous reagent being unnecessary. T. H. P.

Fractionation of American Gum Spirits of Turpentine and Evaluation of its Pinene Content by Optical Means. S. Palkin. (*U.S. Dept. Agric., Tech. Bull. No.* 276, Jan. 1932.)—American gum-spirit of turpentine is obtained, almost exclusively, from the species *Pinus palustris* (longleaf) and *caribaea* (slash pine), and, like that from *P. maritima*, is composed mainly of the isomers α-pinene and nopinene (or β-pinene), the quantities and proportions of which are of commercial importance in the synthesis of camphor and in the manufacture of terpin hydrate. With the possible exception of ozonisation, no quantitative chemical method exists for the differentiation of these isomers, but Darmois, Dupont and others (*Chim. et Ind.*, 1922, **8**, 549, 553, 555; *Bull. Soc. Chim.*, 1923, **33**, 1252; *Bull. Inst. du Pin*, 1929, **60**, 155; **65**, 269) have effected separation, to some extent, by efficient fractional distillation, the proportions of the isomers in the mixtures also obtained being calculated from the rotatory dispersions by the Biot relationship. The present author describes an improved, electrically-heated assembly, comprising a plate rectifying-column with a pressure-regulator and dephlegmator condenser, which was used successfully for the fractionation of turpentine in a vacuum. Fixed pressures (20 and 65 mm.) were used, so that the temperatures of distillation were reasonably accurate indications of approximation of a pure component. The proportions of the isomers in the fractions were determined from the equation X_1 (proportion of α-pinene)$=(a_0-a_2)/(a_1-a_2)$, where a_0 is the rotation of the fraction, and a_1 and a_2 are the rotations of pure α- and β-pinene, respectively. Similarly, beyond the point at which pure β-pinene is obtained, $X_2=(a_0-a_3)/(a_2-a_3)$ where X_2 is the proportion of β-pinene having the rotation a_2, the rotation of the dominant tailings-constituent being a_3. Since differences in density are negligible, actual and not specific rotations may be used. The results shown in the table do not indicate that the increasing use of slash pine as a source of American turpentine will tend to diminish its β-pinene content, the increase of turpentine having a negative rotation, being due, probably, to the nature of the α-pinene, and not to any material change in the proportions of the isomers. No material differences in the total contents of α- and β-pinene were noted, and differences in proportion cannot be ascribed to the variety or to the dip or scrape form of the pine. J. G.

	Rotation (10-cm. tube)				Composition		
Source and sample	a_j (=578mμ)	a_v (=546mμ)	$n_D^{25°}$	$d^{15.6°}$	α-pinene	β-pinene	Tailings
Commercial, from mixed fields of slash and longleaf pine:					Per Cent.	Per Cent.	Per Cent.
1	− 2·4°	− 2·2°	1·4697	0·8707	63·0	31·5	5·6
2	− 9·2	− 9·98	1·4692	0·8662	61·9	32·6	5·3
3	1·9	2·5	1·4680	0·8664	62·2	28·8	6·1
4	− 1·58	−12·58	1·4701	0·8692	59·2	36·9	3·9
Samples from authentic sources:							
Slash pine 3, old	−20·50	−22·56	1·4698 1·4663	0·8667 0·8624	58·0	35·6	6·4
Longleaf pine 1, fresh ..	14·04	16·27	1·4691	0·8680	68·4	28·6	3·0
Longleaf pine 2, fresh ..	12·29	14·34	1·4692	0·8694	62·5	33·3	4·2
Gum dip 8, slash .	−22·58	−24·9	1·4694	0·8657	61·0	33·7	5·3
Gum dip 9, longleaf	11·0	12·86	1·4690	0·8667	62·5	34·4	3·1
Scrape 10, slash .	−25·05	−27·8	1·4700	0·8704	58·8	33·6	7·6
Scrape 11, longleaf .	7·35	8·85	1·4681	0·8675	67·0	29·2	3·8

Empirical Classification of Vat Dyestuffs. C. M. Whittaker. (*J. Soc. Chem. Ind.*, 1932, **51**, 66T.)—The use of 21- and 36-filament 150 denier viscose yarn enables a classification of vat dye-stuffs to be made. Knittings containing 150/21 and 150/36 denier yarns are dyed with the respective dye-stuffs at 20°, 30°, 40°, 50°, and 60° C. Sufficient dye-stuff for five dyeings is vatted at 60° C. with the requisite quantity of sodium hydroxide and "10 per cent. sodium hydrosulphite powder"; the reduced dye-stuff is diluted to a definite volume, divided into five dye baths, and cooled or heated to the required temperature. The amount of liquor is forty times the weight of yarn in each case. The test revealed three types of dye-stuff, which have been classified as A, B and C. A. Those which dye the 150/36 darker at all temperatures; if the 150/21 and 150/36 are about equal in shade at 60° C., the dye-stuff is classified A60. If the 150/36 is still heavy at 60° C. it is classified A60+. B. Those dye-stuffs which dye the 150/36 darker at 20° C., but at 60° C. dye the 150/21 darker. C. Those which dye the 150/21 darker at 20° C., and become increasingly darker on the 150/21 as the temperature is raised. Examples of classification: A60, Caledon Olive R., A60+, Hydron Yellow NF. B30, Alizanthrene Golden Orange G. B35, Paradone Brilliant Violet R. C, Ciba Brown 2R., and Caledon Jade Green. W. P. S.

New Reaction for Dyestuffs containing Copper in Hair and its Use in the Identification of Dye in Hair. H. Meyer. (*Chem. Ztg.*, 1932, **56**, 95.)—A test tube is half filled with a fresh mixture of 10 parts of 10 per cent. hydrogen peroxide, and 1 part of dilute ammonia, and when effervescence has ceased, a few thin strands of hair, 3 to 4 cm. long, are inserted. In the presence of a dye containing copper (*e.g.* henna), bubbles are evolved, and the liquid becomes warm. Other metals and metal-free colours do not react, and cotton or linen fibres containing a copper colour give much weaker reactions than human hair. The reaction is attributed to catalytic acceleration of the decomposition of hydrogen peroxide by copper, in which it is considered that the keratin in the hair plays a part, probably by reason of the physical nature of the protein molecule; a pronounced reaction is, therefore, characteristic of hair. The method may be used in conjunction with micro-modifications of the ordinary reactions of metals for the diagnosis of hair dyes, and a rapid technique, suitable for a sorting test, is described. It is important that the keratin molecule should be sufficiently decomposed in order to obtain the metal in the free state. This is best achieved by the action of cold fuming nitric acid for 3 minutes, after which the solution may be tested for silver by means of hydrochloric acid, for lead by addition of sulphuric acid, and, after neutralisation of most of the acid, for bismuth by the basic nitrate test. For cobalt the hair should be digested for 5 minutes with warm concentrated acetic acid, and the potassium nitrite test applied. J. G.

Determination of Small Amounts of Acids, Alkalis and Salts in Textiles. A. A. New. (*Text. Manufacturer*, February, 1932.)—Small amounts of acid or alkali may be determined by extracting the textile with water (*p*H should be over 6), taking the *p*H value of the extract, and also titrating the extract to an end-point identical with that of the water used for the test. Plotting of the titration results against the *p*H value frequently gives valuable information. The extract is made with 100 c.c. of water for 5 grms. of material for 1 hour, sometimes at room temperature and sometimes at the boiling-point, any loss by evaporation being made good. For commercial work the simple test-paper method still holds its own. For the determination of salts, it is not enough to determine the ash only. An examination should also be carried out of a boiling-water extract, followed by an extraction with dilute hydrochloric acid, and finally with dilute sodium hydroxide solution. These four preparations are tested qualitatively in the usual manner. R. F. I.

Inorganic Analysis

Qualitative Analysis without Ammonium Sulphide. A. S. Komarowsky and W. J. Goremykin. (*Z. anal. Chem.*, 1932, **87**, 339–342.)—The filtrate from the copper arsenic group, boiled free from hydrogen sulphide, is slowly added to a mixture (proportions not stated) of 20 per cent. caustic soda solution, 10 per cent. sodium carbonate solution, and about 5 c.c. of a 3 per cent. hydrogen peroxide; the mixture is stirred during the addition, boiled, and filtered. The filtrate contains zinc, aluminium, and chromate. The precipitate is extracted by boiling with a mixture of ammonium carbonate and ammonia; nickel and cobalt dissolve, the latter as a complex ammine, which must be destroyed by evaporation to dryness with strong nitric acid. The insoluble extraction residue is well washed and dissolved in a little nitric acid and hydrogen peroxide. The solution is approximately neutralised with ammonia, made ammoniacal, treated with solid ammonium chloride and with hydrogen peroxide, and heated to boiling; the precipitate contains iron and manganese. The filtrate is treated with ammonium carbonate as usual for the separation of alkaline earths from magnesium. W. R. S.

Benzidine and Tolidine as Reagents in Analysis. R. G. Harry and E. A. Rudge. (*J. Soc. Chem. Ind.*, 1932, **51**, 64–66T.)—*o*-Tolidine may be substituted for benzidine in testing for the presence of per-salts, aldehydes, etc., but it is more affected by the presence of excess of acid. Both substances give blue colour reactions with manganese, iron, chromium, vanadium, and cerium salts. As little as 1 part of ceric ammonium nitrate in 10,000 parts of water gives a distinct coloration with either benzidine or *o*-tolidine, and the reaction may be used for the colorimetric determination of ceric salts in the absence of manganese, iron and chromium. Lanthanum, thorium, zirconium, yttrium and didymium salts do not yield a coloration with the reagents. Benzidine may be used for the determination of formic acid in lead formate. One grm. of the formate is dissolved in 30 c.c. of boiling water, 6 drops of methyl-thymol-blue solution are added, and 0·2 *N* sulphuric acid is added until the indicator turns bright red in colour; 60 per cent. by volume of alcohol is added, the lead sulphate separated by filtration, the filtrate treated with 8 c.c. of 0·92 per cent. benzidine solution (in alcohol), the precipitated benzidine sulphate separated by filtration, and the formic acid in the filtrate is then titrated with 0·1 *N* sodium hydroxide solution. W. P. S.

Electrolytic Determination of Gallium. E. Reichel. (*Z. anal. Chem.*, 1932, **87**, 321–332.)—The sulphate solution (80 c.c.) was treated with 50 c.c. of strong ammonia and 40 grms. of ammonium sulphate, and electrolysed at 60° to 65° C. between platinum gauze cylinders under agitation (1200 R.P.M.) at 5 amp. and 3·5 volts; duration, 20 to 60 minutes for 0·05 to 0·1 grm. of gallium. As neither the ferrocyanide reaction nor other chemical tests appear to be sensitive enough for ascertaining complete deposition, the electrolysate was tested by repetition of the electrolysis after the cathode had been weighed, any fresh increase in weight being noted. When the electrolysis is interrupted, the cathode is quickly immersed in cold water, washed with water, alcohol and ether, and carefully dried. During electrolysis the metal is liquid and silver-white; when washed it becomes solid and bluish-grey. When the deposit is dissolved in strong nitric acid, the platinum cathode shows signs of alloying, as in the case of zinc. The discoloration after acid attack is best removed by strong heating with a Bunsen burner. Appreciable amounts of platinum are dissolved from the anode, and re-deposited on the cathode. These amounts should be ascertained by blank tests, and the necessary correction applied. The anode, as well as the cathode, should be weighed before and after electrolysis. Further tests are in progress.

W. R. S.

Iodimetric Determination of Chromium and Manganese with Persulphate. J. H. van der Meulen. (*Rec. Trav. chim.*, 1932, **51**, 369–373.)—The conversion of bivalent manganese into permanganate by means of persulphate with a silver salt as catalyst, is normally confined, for quantitative purposes, to relatively small amounts of manganese, owing to the liability of manganese dioxide to precipitate when larger amounts of manganese are present; this precipitation with the larger quantities is prevented if either hydrofluoric acid or phosphoric acid, or both, are present. Silver nitrate acts catalytically in accelerating the oxidation by persulphate of tervalent chromium to chromate, and in securing the rapid decomposition of the excess of persulphate. These facts are used in the following process worked out for determining chromium and manganese when present together in a solution: To 25 to 50 c.c. of the solution (containing not more than 0·05 grm. of manganese and 0·075 grm. of chromium, and slightly acid with sulphuric or nitric acid) are added 15 to 20 c.c. of phosphoric acid (25 per cent.), 2·5 to 3 c.c. of "strong" hydrofluoric acid, 10 c.c. of 0·1 *N* silver nitrate solution, and 1·5 grm. of potassium persulphate. The liquid is heated first on a water-bath until evolution of oxygen bubbles takes place, and then gently boiled for five minutes over a gauze. After cooling, 10 c.c. of *N* potassium iodide solution and 5 c.c. of 5 *N* hydrochloric acid are added; after 2 or 3 minutes the liberated iodine is titrated with 0·1 *N* thiosulphate solution (giving manganese and chromium). To a second similar portion of the original solution are added 25 c.c. of water, 2 c.c. of 0·1 *N* silver nitrate solution, 2 grms. of zinc sulphate, 2 grms. of sodium sulphate crystals, and 1·5 grm. of potassium persulphate. The solution is heated on a water-bath until precipitation of manganese dioxide takes place, and then boiled until the excess of persulphate is decomposed; 5 c.c. of *M* manganese sulphate solution are then added, and the boiling continued until the solution shows no trace of pink colour. The precipitate is filtered off on a sintered-glass filter, washed with hot water, and rejected. Ten c.c. of *N* potassium iodide solution and 5 c.c. of 5 *N* hydrochloric acid are added to the filtrate after cooling; it is kept for 2 to 3 minutes, diluted with 50 to 100 c.c. of water, and the liberated iodine is titrated with 0·1 *N* thiosulphate solution (giving chromium alone). One c.c. of 0·1 *N* thiosulphate solution = 1·7334 mgrm. of chromium or 1·0986 mgrm. of manganese.

S. G. C.

Determination of Boric Acid in Silicates. E. Schulek and G. Vastagh. (*Z. anal. Chem.*, 1932, **87**, 165–172.)—Reliable results may be obtained by the use of the following method. The very fine powder (0·1 to 0·25 grm.; the authors' aim at 0·01 to 0·035 grm. B_2O_3, with maxima of 0·2 grm. SiO_2 and 0·1 grm. Fe_2O_3) is decomposed by fusion with sodium carbonate. After cooling, 5 to 6 c.c. of water are added, and the melt is completely disintegrated by warming. The crucible contents are quantitatively transferred to a distilling flask, and the crucible is rinsed with a minimum of water (total volume of aqueous liquid, 10 to 12 c.c.). The still is connected with a cooler, the exit tube of which dips into 10 c.c. of *N* sodium hydroxide solution, contained in a 250 c.c. silver dish. A cooled mixture of 200 c.c. of methyl alcohol and 15 c.c. of strong sulphuric acid is admitted through a separating funnel, and the liquid is gently heated until all the alcohol has distilled over. The silver dish is lowered, and the cooler tube is rinsed with alcohol. A single distillation suffices for glass and enamels. In the case of ferruginous silicates, the operation must be repeated. The flask is cooled, and 100 c.c. of methyl alcohol, together with a little precipitated calcium carbonate (to prevent bumping) are introduced, and the alcohol again distilled off. The distillate is evaporated to dryness, after addition of 10 c.c. of *N* sodium hydroxide and a few drops of 30 per cent. hydrogen peroxide free from phosphoric acid; the residue is fused (with a little potassium hydroxide, if necessary), and the melt is dissolved in a few c.c. of water, faintly acidified with 10 per cent. hydrochloric acid, and, if cloudy, filtered through a small pad of cotton wool into a 50 c.c. conical flask; three washings with water in 2 c.c.-portions are applied. The filtrate (15 to 20 c.c.) is boiled for one minute with coarse pumice powder to expel carbon dioxide, cooled and neutralised with 0·1 *N* alkali against a drop of methyl red indicator. After addition of 2 grms. of pure mannitol and 5 drops of phenolphthalein, the liquid is heated to boiling, and titrated with 0·1 *N* alkali to the first tint of pink. This must persist after addition of 0·5 grm. of mannitol (1 c.c. = 0·003482 grm. B_2O_3). The residual liquid in the still should be tested for complete elimination of the boric acid by another distillation with 30 c.c. of the alcohol and repetition of the above procedure. Complete recovery was effected by single distillation in most cases, and by double distillation in all. A micro-method for 0·0007 to 0·003 grm. B_2O_3 is also described; it follows the lines of the procedure here reproduced. W. R. S.

Microchemical

Vacuum Sublimation under the Microscope. L. Kofler and W. Dernbach. (*Mikrochem.*, 1931, 9, 345–349.)—A simple apparatus for observing sublimation *in vacuo* under the microscope is made for use with the micro melting-point apparatus of Klein (*Mikrochem. Pregl-Festschrift*, 1929, 192), or with that devised by Kofler and Hilbck (*Mikrochem.*, 1931, 9, 38). It consists of a square microscope slide, with sides 3½ cm. long. A cover with walls, 6 mm. high, in which is blown a side tube to connect with the vacuum pump, is cemented on to the slide. The top of the cover must be parallel in plane to the slide to avoid distortion of the image. The substance to be sublimed is placed on the slide, and the sublimate is collected on a cover slip, held at a distance of 4 mm. from the slide by means of a small glass or metal ring. The cover slip and metal ring should fit conveniently under the vacuum cover. The whole apparatus is placed on the melting-point apparatus. J. W. B.

Micro-Determination of Carbon by the Wet Method. (Part II). Combustion of Liquids. E. Schadendorff and M. K. Zacherl. (*Mikrochem.*, 1932, 10, 99–108.)—The micro-method of Lieb and Krainick (*Mikrochem.*, 1931, 9, 367; ANALYST, 1932, 273) is extended to the combustion of liquids. The method is the same except for the manner of introducing the weighed sample into the combustion chamber. Liquids with a boiling point above 200° C. can be weighed into an ordinary Pregl combustion boat, and placed in the oxidation chamber. Liquids of lower boiling point are weighed into small capillary tubes, 1 mm. in diameter, with a small solid handle at one end, and sealed. The length of capillary and handle is 4 cm. In order to break the capillary inside the oxidation chamber, the vessel is made slightly pointed, instead of rounded at the bottom, and two small lumps of glass, one above the other, serve to support the capillary in a vertical position when it is dropped, handle downwards, into the vessel. The gas inlet tube is made with a projection at one side, about 1 mm. from the opening, which is about 1·5 cm. from the bottom of the vessel. By rotating the inlet tube the capillary is very simply broken. This is done after the chromate mixture has been added and the baryta introduced into the absorption vessel. Nine different liquids were tested, and excellent results were obtained. The method was also tested on solutions; 0·3 per cent. aqueous solutions of urea gave unsatisfactory results, usually low, but synthetic mixtures of urea, uric acid, hippuric acid, and creatinine in water, in similar proportions to those present in urine, gave good results, with a maximum error of 3 per cent. Determinations were also made on blood serum, and the results agreed with those obtained by the dry combustion (Pregl) method. J. W. B.

Microchemical Determination of Glucose. Ch. Cimerman and P. Wenger. (*Mikrochem.*, 1931, 9, 295–299.)—The method is suitable for concentrations of glucose of the order of 0·1 to 1 per cent. Fehling's solution is used, the precipitate is centrifuged instead of filtered, and the whole procedure is carried out in one tube. A preliminary determination should be made, and the test solutions appropriately diluted to a concentration of 1 or 0·1 per cent. *Reagents.*—Two copper sulphate ($CuSO_4, 5H_2O$) solutions, containing, respectively, 34·65 grms. in 500 c.c., and 69·30 grms. in 500 c.c. Two sodium potassium tartrate solutions, containing, respectively, 175 grms. of tartrate and 50 grms. of sodium hydroxide in 500 c.c., and 17·5 grms. of tartrate and 5 grms. of caustic soda in 500 c.c. Approximately 0·5 per cent. solutions of guaiacum in alcohol and potassium cyanide in water. *Method.*—For approximately 1 per cent. solutions of glucose the more concentrated copper sulphate and tartrate solutions are used, and for 0·1 per cent. solutions the more dilute; 2 c.c. of copper sulphate solution, and 2 c.c. of the tartrate solution are placed in the reagent glass of 40 c.c. capacity, with an exterior diameter of 3 cm. The solution is heated to boiling, and the sugar solution is added from a burette until decolorisation is apparent. The tube is then centrifuged for 1 or 2 minutes at a velocity of 2000 to 2500 revolutions per minute. A small drop of the clear liquid is tested for copper by placing it on a filter paper, followed by a drop of the guaiacum solution, and a drop of the potassium cyanide solution. A blue colour indicates copper. When copper is still present, more sugar solution is added, and the solution is again heated to boiling and centrifuged. The method eliminates the possibility of oxidation during filtration, and gives results accurate to a few units per cent. on 0·1 per cent. solution of glucose. Ions that react with potassium cyanide ($Hg^{\cdot}$, $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$), or with guaiacum ($Pb^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$), should not be present. Lead may be removed by adding potassium carbonate to the test solution before the determination. J. W. B.

Dry Method for the Micro-Analysis of Gases. F. E. Blacet and P. A. Leighton. (*Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 266–269.)—An apparatus for the micro-analysis of gases is described, together with a method for the analysis of gas samples of the order of 25 to 100 c.mm. without the use of liquid reagents. Yellow phosphorus is used to remove oxygen, fused potassium hydroxide for carbon dioxide and fused phosphorus pentoxide to remove water vapour. These absorbents are also used in the analysis by combustion of hydrogen, carbon monoxide and methane. The volume of gas is measured in a water-jacketed micro-burette made from a capillary tube about 0·5 mm. in diameter, and accurately ruled in mm. divisions for a length of 45 cm. It is calibrated by weighing drops of mercury; the capacity is approximately 1 c.mm. for 4 linear mm. The lower end of the tube is sealed to a larger tube, containing a trap to keep out any impurities from the capillary during sealing, and this is attached to a short length of heavy rubber tubing, which is filled with mercury and plugged, and clamped in a heavy clamp with a finely-threaded screw, by means of which the level of mercury in the burette may be adjusted. The upper end of the capillary is bent down, and ends in a tip of small outer diameter, which is turned up, and is submerged in mercury in a small reservoir (7 cm. in diameter), which can be raised or lowered. The containers for the gas samples have a capacity of 2 c.c.; they are inverted, and are attached by means of circular steel springs to a revolving table, so that their position can be easily adjusted. For the determination of oxygen in dry air the containers are filled with mercury and then several hundred c.mm. of the gas are added from a glass tube drawn out to a capillary, or by means of a Toepler pump. The burette is next completely filled with mercury, and the tip is brought into the gas sample, and 25 to 100 c.mm. are drawn in by means of the screw, after which further mercury is drawn in, the tube being tapped to prevent sticking, and the volume of gas is read in the calibrated part of the tube. The mean of five independent readings should be taken. The gas is then expelled into a second container, and the oxygen is absorbed by yellow phosphorus, which has been fused into a loop of platinum, and kept under mercury. The platinum wire has a glass holder, by means of which the phosphorus may be placed in position in the holder containing the gas, so that only the phosphorus bead and a little platinum wire enter the gas bubble, without touching the sides of the holder. In most cases the gas is completely absorbed in 15 minutes, but it is safer to draw the residual gas into the burette, take a reading, and again expel it, and allow it to remain in contact with the absorption agent for a further 5 minutes, until the volume is constant. For the absorption of water a bead of fused phosphorus pentoxide, prepared over a glowing electric coil, is used; carbon dioxide is absorbed by fused potassium hydroxide, also prepared over an electric coil, but allowed to collect moisture from the air until the surface is shiny, before it is placed under the mercury in the reservoir. Errors in test determinations were usually less than 1 per cent. J. W. B.

Mill for Small Samples. W. H. Cook, E. P. Griffing and C. L. Alsberg. (*Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 102–106.)—A mill suitable for grinding individual wheat leaves and grains, without loss of substance and moisture, is designed on the general cutting principle of the Wiley laboratory mill (*Ind. Eng. Chem.*, 1925, 17, 304). A rapid shearing effect is obtained by the action of a hard tooled steel knife with four blades keyed to a shaft, cutting against one blade of tooled steel placed in the wall of the grinding chamber. The rotating knife also serves to keep the material in motion, and when it has been ground sufficiently, aids in its discharge through a screen in the bottom of the chamber. The main body of the mill consists of a cast-iron block, 2 inches square and 4 inches long, $3\frac{1}{2}$ inches of which are occupied by the bearing for the half-inch shaft. The front half-inch forms the grinding chamber, which is $1\frac{1}{4}$ inches in diameter, and the rotating knife, keyed to the shaft, occupies about three-quarters of its capacity. The length of the rotating blades from the centre of the shaft is $\frac{1}{2}$ inch. A brass tube, $\frac{7}{16}$ inch in diameter, leads into the top of the grinding chamber for introducing the material, and is closed during grinding by means of a solid brass piston. The bottom of the chamber is formed by a copper drawer where the ground material is collected; the top of the drawer consists of a mesh of the desired size. A water-cooling system surrounding the shaft prevents overheating of the material, but may be dispensed with. The capacity of the mill is 5 to 8 kernels of wheat, which are best ground up a little in a mortar before grinding in the mill, and leaves are cut into small pieces. At an operating speed of 5600 rotations per minute, and a clearance of 1/2000 inch between the rotating and stationary blades, a single charge of material is reduced to pass an 80-mesh sieve in from 3 to 4 minutes, and gives a homogeneous sample. (Made by A. H. Thomas & Co., Philadelphia.)

J. W. B.

Micro-Gravimetric Determination of Silica in Tissue. J. C. Morgan and E. J. King. (*J. Biol. Chem.*, 1932, **95**, 613–620.)—The results are given of an attempt to develop a micro-gravimetric method for the determination of silica. The procedure evolved is based on the same chemical principles as the usual gravimetric analysis for silica, but the technique is entirely different. In working out the method, use was made of the apparatus and methods described by Emich [*Lehrbuch der Mikrochemie*, Munich, 2nd edition (1926); *Mikrochemisches Praktikum*, 2nd edition (1931)] and by Pregl (*Quantitative organic microanalysis, translated by E. Fyleman*, London, 2nd edition, 1930, 6, 16); a micro-balance is essential. The precautions necessary and the difficulties encountered are described in detail. The samples of tissue were ashed to remove organic matter by means of ring burners. It was decided to volatilise the silica with hydrofluoric acid, and then determine the silica from the loss in weight on volatilisation. An attempt was made to ash the tissue and treat the ash directly with the hydrofluoric acid, without separating the silica from the other non-combustible substances. However, on addition of acids, the salts formed showed a marked tendency to creep up the sides of the crucible and over the edge, whatever the mode of heating. Therefore, the procedure finally adopted was to ash the tissue, render the silica insoluble, filter off the other substances, and treat the purified silica with hydrofluoric acid. The method of rendering silica insoluble is simply to heat it in acid solution, which at the same time dissolves practically all other material present. The acid commonly employed is hydrochloric, but a more satisfactory agent was found in the dihydrate of perchloric acid, which is a powerful dehydrating agent at its boiling-point, 203° C. By boiling the silica for 15 minutes with perchloric acid, the dehydration is completed, and the mixture does not require to be evaporated to dryness. After cooling, and the addition of silica-free distilled water, the solution is filtered off. The transference of the precipitate from the crucible was avoided by the method of filtering evolved by Emich, which consists in sucking off the solution through a filter stick. An illustration shows the manner in which this was used. The filter paper left in the crucible was dried, then burned off, leaving the silica in the crucible in a fairly pure state. Its weight was determined by heating until fuming ceased, first with sulphuric acid, and then with hydrofluoric acid *plus* sulphuric acid, the crucible being weighed after each operation. The ring burners used heated the top part of the crucible uniformly by means of flames radiating horizontally inward from a ring surrounding the crucible; they gave a blue flame which could be regulated from the merest glow to a length of one inch. A few typical results are given. The time required to make duplicate determinations on two tissues (four crucibles) was about 8 hours.

P. H. P.

Physical Methods, Apparatus, etc.

Use of Saturated Ammonium Chloride in the Elimination of Contact Potentials. C. N. Murray and S. F. Acree. (*Bureau of Standards, J. Res.*, 1931, 7, 713–721.)—In *p*H and potentiometric determinations it is usually necessary to allow for or eliminate the small potential difference between electrode liquids of different compositions by (1) calculation (which can, however, only be used in the comparatively few cases where data are available); (2) experimental measurement of the potential; or (3) elimination of the potential by the insertion of a "bridge," composed of a solution of an electrolyte, the ions of which have almost equal mobilities. In case (3) potassium chloride is usually employed, but the authors have tested solutions containing ammonium chloride, since this salt has a higher solubility than potassium chloride, and its ions are almost equal to one another in mobility. Comparisons were made with a new form of double hydrogen electrode-cell, which is described, a dye being added to facilitate observations of the movement of the liquid junctions. It is concluded that solutions of ammonium chloride up to the saturation-point (5·66 *N*) are preferable to potassium chloride, particularly for solutions of low *p*H value, and annul the contact potential to within ± 1·0 millivolt. Mixtures of ammonium or potassium chloride and nitrate in a molar ratio of 1:3 are also satisfactory for solutions of *p*H 3 to 10, since they are stable and the nitrate counterbalances the effect of the slightly higher mobility of the chloride ion. An error of 1 to 2 millivolts, in saturated calomel electrodes, may arise, through the customary use of a layer of potassium chloride crystals over the calomel, and the resulting hysteresis in solubility and potential when the temperature fluctuates; 4 *N* potassium chloride solution (*i.e.* a saturated solution without solid crystals) should, therefore, be employed when the electrode is not used in a thermostat (*cf.* following abstract). J. G.

Estimation of Liquid Contact Potentials with Potassium Chloride and Ammonium Chloride. G. M. Kline, M. R. Meacham and S. F. Acree. (*Bureau of Standards, J. Res.*, 1932, 8, 101–110.)—The Bjerrum method of correction for contact-potential by extrapolation is liable to errors of 1 to 3 millivolts if used outside the limits (*e.g.* of concentration) set by Bjerrum. The results have, therefore, been compared with those obtained by the Loomis–Acree method (*cf.* Noyes and Ellis, *J. Amer. Chem. Soc.*, 1917, **39**, 2532), in which 4·1 N (saturated) potassium chloride solution is used, by means of the systems HgCl | 0·1 N KCl | xKCl | 0·1 N HCl–H_2–Pt, and also of systems in which organic acids and acid salts replace the highly ionised hydrochloric acid. The Loomis–Acree method was shown to have greater accuracy, simplicity and rapidity, and being based on experimental results, it avoids the use of uncertain extrapolations. It is, therefore, recommended for general use in order to ensure uniformity of published data, an approximately isoelectric eliminator, such as (3 N KCl + N KNO_3), being suitable for solutions of *p*H 3 to 10 (*cf.* preceding abstract). J. G.

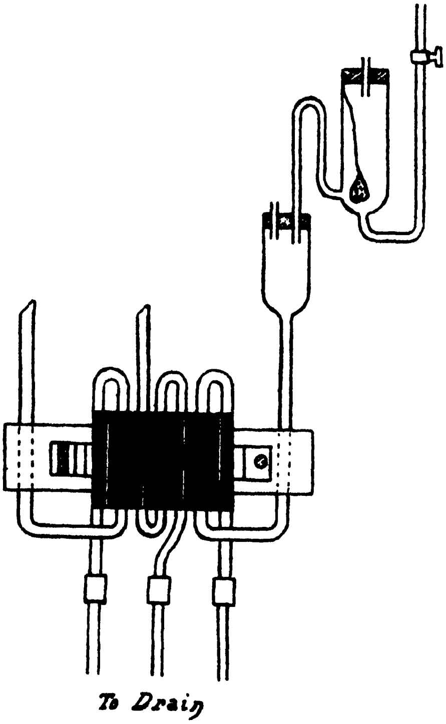
Ventilation of Vehicular Tunnels with Particular Reference to those at Blackwall and Rotherhithe. C. J. Regan. (*London County Council, Annual Report of the Council,* 1930, **4**, Part III. *Public Health—Medical Supplement to the Report on the Hospital Services,* pp. 271–281.)—The exhaust gases from the majority of motor vehicles contain 5 to 9 per cent. of carbon monoxide, but the actual proportion may vary considerably outside these limits, according to the conditions. After consideration of all the pertinent factors, such as the facts that men may be employed on maintenance work for several hours at a stretch, and that long exposure to low concentrations of the monoxide causes far more tissue damage than short exposure to high concentrations, it was deemed advisable that the carbon monoxide content of the air of tunnels, such as those of Blackwall and Rotherhithe, should not be allowed to exceed 20 parts per 100,000.

The following methods were used for analysing the air: (1) The carbon monoxide was determined by Teague's method (ANALYST, 1920, **45**, 459). (2) The suspended matter was determined by means of Owens's portable air-filter, a measured volume of the air being drawn through a small circle of a porous paper disc, and the depth of colour of the circle then compared with a series of shades, one unit of which represents 0·32 mgrm. of black suspended matter per cubic metre of air. It was decided that the average shade of three successive samples taken at short intervals, at any point in the tunnel, should not exceed 6 (1·92 mgrm. of black suspended matter per cubic metre). The actual number of suspended particles was determined with Owens's jet dust counter, a fine ribbon-shaped jet of the moistened air impinging on a microscope cover-glass about 1 mm. in front of the orifice of the jet. The adherent dust particles were then counted under the microscope. (3) Humidity was measured by means of a standard Assmann wet and dry bulb hygrometer. (4) The acidity and sulphur dioxide were determined by passing known volumes of the air through (*a*) hydrogen peroxide solution, and subsequently titrating with alkali, and (*b*) iodine solution, and then titrating with sodium thiosulphate.

In both tunnels, atmospheric conditions are worst at about 10 a.m., and are also worse in summer than in winter, particularly when the temperature of the open air rises above that of the tunnel air, and so decreases natural ventilation. When the average open-air temperature during the 24 hours is above 58° F., the average humidity in the tunnel (for the 24 hours) rises above that of the open air;

otherwise the reverse is normally the case. In no case did the humidity in the tunnel become 100 per cent., so that any foggy conditions which arise are due to smoke fogs, and not to water-vapour fogs. T. H. P.

Automatic *p*H Recorder. **C. Morton.** (*J. Soc. Chem. Ind.*, **1931**, **50**, 436–438T.)—The annexed diagram is an additional illustration to the abstract of this paper. (ANALYST, 1932, 201.) J. G.



Reviews

OFFICIAL AND TENTATIVE METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. Compiled by a Committee. Third Edition, 1930 (received December, 1931). Pp. xvii + 593. Published by the A.O.A.C., Washington.

There is no other book quite like this one in the whole range of analytical chemistry. It is essentially a practical treatise—a book for the laboratory bench—and one must not, therefore, expect literary style, nor, indeed, allow one's self to be irritated by the numerous contractions adopted throughout the work. It is a book of methods. It contains no standards, no limits of composition, no typical analyses, and no recommendations other than recommended methods. Its outstanding feature is clarity of composition, and that is of vital importance in such a compilation. In view of the origin of this book, moreover, no objection can be taken to the occasional use of phonetic spelling.

The aim of the work is to include all the approved methods of the Association for the analysis of agricultural products, and of related substances of importance in agriculture. As is stated in the Preface to the Second Edition, "The methods are the outgrowth of continual critical and collaborative trial . . . participated in by a large number of workers, and undertaken in order to establish the accuracy of analytical results. . . . They are formulated solely by responsible Federal and State officials, acting together, and thus are based on underlying principles of equity. . . ." These methods have consequently been accepted as authoritative in matters at issue before the Federal and State courts in the United States of America. The book sets out to do for American chemists, over a large range of materials, what the Standing Committee on the Uniformity of Analytical Methods of our Society is doing for a limited number of specific products.

A compilation of such authoritative methods, if well done, must have a unique value, and it may be said at once that the work has been ably planned and the scheme most carefully and successfully carried out. The result is a book which no food chemist or agricultural chemist can afford to ignore, and, indeed, the earlier editions of the book are well-known to British workers. It is true that the restriction of the included methods to those of agricultural products—albeit this term is widely interpreted—results in some curious admissions and omissions, but the latter are to be remedied in future editions.

The subject-matter of the book is broadly grouped into two main divisions, the new chapters being denoted here by italics:—NON-FOODS.—Soils; Fertilisers; Agricultural Liming Materials; Insecticides and Fungicides; *Caustic Poisons*; *Naval Stores*; *Paints*; Leathers; Tanning Materials; Plants. FOODS.—Baking Powders; Beverages; Beers, Wines and Distilled Liquors; Coffee and Tea; Cacao Bean and its Products; Cereal Products; Coloring-Matters in Foods; Dairy Products; *Eggs and Egg Products*; Flavouring Extracts; Fruits and Fruit Products; Grain and Stock Feeds; Meat and Meat Products; Metals in Foods; Oils, Fats and Waxes; Preservatives and Artificial Sweeteners; Spices, etc.; Sugar and Sugar Products; and Vegetables and Vegetable Products. There are also chapters on Waters, *Radio-activity*, and Drugs, and 69 pages of tables of reference. The food section of the book (283 pp.) is conveniently arranged in alphabetical order. It is intended in the future to take up similar work in connection with Sewage; Paper; Fibres; Fish; Nuts and Nut Products; Vitamins; and Bacteriological and Microchemical Methods.

The chapter on Soils, though short, is of note, and under the section on the determination of reaction values there are given the pH equivalents in arithmetically-related numbers. Fertilisers are dealt with in 18 pages, and methods for the determination of boric acid are given. The official methods for the determination of potash all involve the use of platinum chloride. There is an excellent chapter of 31 pages on Insecticides and Fungicides, including methods for the determination of arsenic in its various forms in substances such as Paris Green, London Purple, Bordeaux Mixture, and in lead and magnesium arsenates. Methods of analysis of cyanide compounds, of tobacco and extracts of tobacco (in which nicotine is determined by the silico-tungstic acid method), and of products containing mercury and fluorine, are also included.

In the Foods section of the book, some of the methods familiar to British chemists are given in altered form. The Reichert–Meissl process is carried out by distilling, without first melting the fatty acids, during thirty minutes, and other details of the method differ from the standard process as used here. It may be important to remember this when comparing results obtained in the two countries. The determination of arsenic in meat foods is made by precipitating the magnesium ammonium arsenate and phosphate together; and, after solution of the precipitate in hydrochloric acid, the arsenic is evolved in a modified Gutzeit apparatus, recently-impregnated mercuric bromide papers being used. The presence of aluminium salts in baking-powders is detected by the use of aurin-tricarboxylic acid, which forms a lake with the aluminium salt, and gives a bright red precipitate on addition of ammonia. Artificially-coloured wines, which are notoriously difficult to titrate with an internal indicator, are examined for acidity by making use of a mixture of powdered phenolphthalein and potassium sulphate (1:100) employed as an external indicator.

The book contains a valuable chapter on Colouring-Matters in Foods, including the identification of the dyes and their examination for impurities. The official methods for the determination of added water in milk include the measurement of the refractive index of the serum, on both the fresh and the sour samples, and also the cryoscopic method, of which a very full account is given. A useful qualitative test for mineral acid in vinegar is one employing methyl violet, which gives, with the diluted vinegar, a blue or green colour in the presence of such an adulterant. The methods for the determination of the amount of benzoic acid in foods, depending on solution in chloroform, appear to be simpler and more rapid than some methods in use in this country, and are worthy of trial. Lastly, mention may be made of the micro-chemical tests for the alkaloids, which are described in the section on Drugs. There is a good Index.

Very few errors have been noticed, and most are of a trivial nature; some of them were corrected (as errata) before the book was sent out. The volume, as a whole, has been carefully produced, and the subject-matter is well arranged and copiously cross-referenced. It should be on the bench of every analyst who has to examine the materials dealt with in this compendium of agricultural analytical methods, and, once brought into use, it will rapidly become a much-consulted companion.

ARNOLD R. TANKARD.

SOIL CONDITIONS AND PLANT GROWTH. By Sir E. JOHN RUSSELL, D.Sc., F.R.S. The Rothamsted Monographs on Agricultural Science. Sixth Edition. Pp. vi+636, with Illustrations. London: Longmans, Green & Co. 1932. Price 21s.

One of the most active branches of agricultural science during the present century has been that dealing with soils. Great advances in our knowledge have taken place in a comparatively short space of time, and since the great war soil workers in this country have been greatly influenced by the views of continental, and especially of Russian, workers. A number of international Conferences have been held, which have brought together soil investigators from all over the world, and many British workers have attended either the sectional Conferences, held from time to time, or the great international congresses, which were held in the United States in 1927, and in Russia in 1931. The result has been a widening of our point of view, and we are no longer in danger of supposing that we can generalise from the soils of the south-east of England to the wide world, or even to the soils of the British Empire, which cover a wider range of climatic and other conditions than those of any single country. This widening of the outlook of British soil scientists is reflected in the new edition of Sir John Russell's great work on Soil Conditions and Plant Growth, which is in many sections a new work. It is not only greatly enlarged compared with the previous edition, but it exhibits clearly the benefits which accrue to workers in soil science from international travel and international congresses. Sir John Russell took part in both the international congresses already mentioned, and he has travelled extensively in the widespread countries of the Empire, and the great experience and knowledge he has gained of the soil conditions of the world are placed at the service of the readers of this work.

The first edition of Soil Conditions and Plant Growth was published twenty years ago as one of the Monographs of Biochemistry, and was a small volume of 168 pages, not much more than one-quarter the size of the present volume. The demand for a work of this kind was shown by the issue of a new impression less than a year later, and by the issue of new editions in 1915 and 1917. All of these issues represented the somewhat narrow British view of soils in which the classical soil of Rothamsted was the centre of the picture, and the soils of the south-east of England filled in practically all the rest. In 1921 and 1927 the fourth and fifth editions were published in the series of Rothamsted Monographs on Agricultural Science, and this new (sixth) edition is in the same series. In these editions the work has been gradually altered and increased, and the present edition is very different in treatment, content and outlook from the early editions.

The general arrangement is somewhat similar to that of the last edition, and the number of chapters is the same, but the Washington and Russian congresses of the International Society of Soil Science have taken place since that volume was issued, and these have had their effect. Large sections have been added which were not in the fifth edition, and many of the old sections have been re-written and re-arranged.

As in all the previous editions, the book opens with a historical chapter, the only chapter that is practically unchanged. The second chapter is on "Soil Conditions affecting Plant Growth," and, though the title is unchanged, the text has been re-arranged and much extended. The third chapter deals with "The Composition of the Soil," and it also has undergone much amendment and extension. Some account of the views of Wiegner and other colloid chemists on the colloid constituents of the soil has been introduced, and all the treatment of soil acidity has been altered and modernised. The section on soil organic matter has been added to, but, though there are further references to the subject in Chapters V and VIII, much recent work on peat and peat soils has not been included. There is a new section on the structure of the soil at the end of this chapter, but this might better have been taken after Russian views on soil profiles and soil types had been dealt with in the following chapter. This is a very long chapter, and is greatly improved as compared with the previous edition.

The next two chapters have new titles, and IV, now called "The Soil in Nature; Changes in its Mineral Composition," is practically a new chapter. The Russian climatic classification of soils is given, and the Russian nomenclature is adopted to a large extent. Soils are classified into wide belts from a world point of view, according as the climate is hot or cold, humid or arid, and the effects of ground water, topography and vegetation are all considered. Chapter V deals with changes in soil organic matter, and Chapter VI, the title of which is unchanged, deals with the closely related subject of the "micro-organic population of the soil." These chapters are not so much altered, though a considerable amount of new matter, derived from the investigations at Rothamsted and elsewhere, has been introduced. Among interesting new facts, it is stated that four new species of nitrifying organisms, "differing completely from *Nitrosomonas* and *Nitrosococcus*," have recently been discovered at Rothamsted. In this chapter on micro-organisms are included sections on worms and other quite visible invertebrate organisms. The titles of Chapters VII and VIII are unchanged, and a good many of the sections are the same as, or similar to, those in the previous edition, but a considerable amount of new matter is given, such as an account of Dr. Keen's work at Rothamsted on Drawbar pull and its relations to the moisture and calcium carbonate content of the soil. In these chapters the author, in striving after completeness and the inclusion of everything, has included a mixture of analytical matters and questions of nomenclature and soil type, which one would naturally look for in other sections of the book. The concluding Chapter IX is very short, only 7 pages. It is a contrast to all the others in this respect, for they have all been lengthened, while this one has been cut down to less than half. It deals with soil surveys and soil maps, a subject which has been occupying an important place in recent soil meetings and congresses, and on which much more work has been done all over the world than might be supposed from the very slight treatment it receives here.

Soil Analysis, chemical, mechanical and bacteriological, occupies an Appendix of 19 pages. This gives an epitome of the methods usually followed in this country, the methods given being those of the Agricultural Education Association, where such exist.

As in previous editions, a feature of the work is the selected bibliography, in which the authors are arranged alphabetically, and the pages in the text given on which their work is referred to. In addition to this bibliography, which is of great value to the student of soils, very complete references are given throughout the work to the original authorities relied upon for the statements made in the text. The work ends with an index of authors and subjects.

This is a work which contains a mass of information from world-wide sources on the fundamental subject of the soil and its relations to plant life and growth. It is a book which no agricultural teacher or soil investigator can afford to be without. The subject is one in which an immense amount of investigation is being carried out in many countries by chemists, physicists, and biologists, and which is rapidly advancing. No doubt another new edition will be required before many years are past; the subject is now such a vast and varied one, that the reviewer would venture to suggest that the work should either be divided, or that different specialists should become responsible for the production of different sections.

JAMES HENDRICK.

HANDBUCH DER PFLANZENANALYSE. By G. KLEIN, Vienna and Heidelberg. Zweiter Band. Spezielle Analyse. Erster Teil. Anorganische Stoffe. Organische Stoffe I. With 164 illustrations. Pp. 973. Published by Julius Springer, Vienna. 1932. Price unbound, RM.96.

The modern tendency towards specialisation has brought in its train the production of a plethora of books dealing with the chemical methods required in the study of one or other branch of science; such books may be justified on the ground that they save workers in any particular field the time and trouble involved in searching for these methods in separate books, but, on the other hand, the attempt to get all requisite information under one cover, results in the production of rather unwieldy volumes. The book under review is adapted to the needs of those engaged in the analysis of plant materials, and is a compilation in the production of which twenty-three authors have taken part. As may be seen from the title, it forms the second volume of the "Handbuch," and contains only the first part of the section devoted to Special Analysis; as such, it is concerned with inorganic substances, and some only of the organic substances occurring in plants; among the organic substances dealt with are included the alcohols, aldehydes and ketones, phenols and quinones, acids, phosphoric esters of carbohydrate metabolism, lipoids, fats and waxes, phosphatides, phytosterols, sugar alcohols, sugars, and polysaccharides.

Though written by different authors, the sections are similar in general arrangement, and include, in most cases, histological or microchemical methods of investigation. A great many references to original sources are given, and, on the whole, these are well chosen, though individual differences of opinion are bound to occur as to the selection. A special feature is the inclusion in most sections of an account of the occurrence and distribution of the substances dealt with in the various families and genera, written by such an experienced authority as Professor Wehmer. The first part of the book, devoted to inorganic substances, occupies 202 pages, and includes sections on the analysis of the more important kations and anions, on the detection and estimation of ammonia, nitrate and nitrite, on ash analyses in general, and on gas analysis, including both macro- and micro-methods. The book contains a number of illustrations of apparatus and of crystals, etc., and no pains or expense have been spared to make it as nearly complete as possible.

With so much that is excellent, there would seem to be little justification for criticism, but it is difficult to refrain from wondering whether, for example, some of the details of inorganic analysis could not have been left out; so many excellent text-books deal with this subject already. On the other hand, in connection with the descriptions dealing with the occurrence of the sulphate group in plants, we look in vain for any mention of the existence of the carbohydrate esters of sulphuric acid, which have been shown to be important cell wall constituents of both the red and the brown algae; in this connection it is also worthy of note that another cell wall constituent of the brown algae—mannuronic acid—likewise finds no mention. As a book of reference, this volume is likely to be appreciated by all engaged in the investigation of plant constituents and plant metabolism.

P. HAAS.

ERGOT AND ERGOTISM. A Monograph based on the Dohme Lectures delivered in Johns Hopkins University, Baltimore. By GEORGE BARGER, F.R.S. Pp. xvi+279. London and Edinburgh: Gurney & Jackson. 1931. 15s.

There were advantages in living in England, even in the Middle Ages, and one of them was that our people never took kindly to rye, so that this cereal did not become a staple bread-corn, and they escaped the horrors of ergotism. Even Professor Barger's penetrating search into the history of outbreaks of this disease has revealed only one occurrence of typical gangrenous ergotism, near Bury St. Edmunds, in 1762, which was confined to one family, and was possibly due to ergotised wheat, a similar single case in Liverpool, in 1923, due to eating rye-bread, and a mild, but more extensive, outbreak of convulsive ergotism in Manchester in 1927–1929, among a colony of immigrants from Central Europe, who ate bread composed of one part of rye-meal with four parts of wheaten flour. This rye was grown in South Yorkshire, and Professor Barger estimates that the loaves made from it must have contained about 5 grms. of ergot per half-pound loaf.

Owing to this immunity from ergot poisoning, professional interest in this fungus in England has been confined almost entirely to its use as a drug, and, even on this side, has been limited by the fact that ergot and its preparations in the British Pharmacopoeia have not been controlled by any analytical standards. This state of things needs alteration, and if the special Sub-Committee on ergot is successful in getting the recommendations of its recently-issued report adopted, the ergot preparations of the new Pharmacopoeia will at long last be made and controlled in accordance with the new knowledge of ergot, which has accumulated since the discovery of ergotoxine in 1906.

Professor Barger is one of the principal contributors to our knowledge of this drug, and the preparation of this very complete account of ergot and ergotism is not the least of his services in this direction. For analysts the most interesting section will be Chapter VI, dealing with the pharmaceutical and forensic aspects of ergot. This begins with an excellent comparative and critical summary of the treatment of ergot in nineteen different pharmacopoeias, and then proceeds to discuss processes of chemical and biological assay. The quality of ergot is next dealt with, followed by a discussion of the stability of the active principle in the natural drug and in the liquid extract and other preparations, and ending with an article on "ergot and public health," which includes a summary of methods for the detection and estimation of ergot in flour and bread.

Stress is naturally laid in a review in this Journal on the portions of the volume of particular interest to analysts, but it should be added, since analytical work can only be successfully conducted on a basis of sound knowledge, that the book contains a wealth of information on the history of ergot and ergotism, and on the botany, chemistry and pharmacology of the drug. The labour involved in the preparation of the volume must have been enormous, and chemists, pharmacists and medical men should be grateful to the author for so interesting and complete a presentation of the subject.

The issue of books like this is of no small public service, and it is to be hoped that the enterprise of the publishers will be rewarded by a larger circulation than that provided by the small public to whom the title "Ergot and Ergotism" is likely to make an immediate appeal. T. A. HENRY.

VEGETABLE FATS AND OILS. By GEORGE S. JAMIESON, Ph.D., Chemist in Charge of Oil, Fat and Wax Laboratory, Bureau of Chemistry and Soils, United States Department of Agriculture. Pp. 444. New York: Chemical Catalog Company, Inc. 1932. Price $6.50.

The editors of the American Chemical Society's series of monographs have been fortunate in inviting Dr. Jamieson to undertake this volume on the chemistry, production and utilisation of vegetable fats and oils, since he is one of the foremost authorities on this subject in the United States. He himself has made notable contributions to recent extensions of our knowledge of natural fats and, still more to the point, he has developed the subject in this book in an exhaustive, modern and accurate manner.

It is not easy to know where to begin with a topic which presents so many angles of approach. Usually one finds, first, an account of the fatty acids, alcohols, etc., which occur in combination in natural fats, then descriptions of how these may be characterised and estimated, and so on, until finally, the ground having been cleared, the description of the fats themselves is reached. Dr. Jamieson, on the contrary, devotes sixteen pages to a rapid, but extraordinarily good, survey of what fats are, where they are found, how and why (in so far as is known) plants and animals produce them, how they are extracted and refined, their nutritive value, and matters such as rancidity and emulsions, and then embarks at once on a description of all the technically important and many of the at present less utilised vegetable fats (255 pp.). The concluding chapters deal with the component fatty acids and alcohols, and also (very fully) with methods of analysis and detection. Naturally, in the brief introduction mentioned, no attempt is made to go into any detail; but different phases (for example, extraction, refining, hydrogenation) are discussed very fully in connection with one or other fat, usually that with which each such phase is most closely connected in American practice, Thus, extraction is dealt with under various oils, refining, especially in the cases of cottonseed, linseed, olive and some others, whilst hydrogenation is included in the cottonseed oil section. Individual taste must largely determine which form of treatment is preferred; the writer can only say that, to him, the method adopted is refreshingly novel, and perhaps more interesting than the more conventional plan. It must be added, however, that a book written on these lines requires ample indexing, with adequate cross-references, and that, in this respect, the existing index should be much extended in order to render rapidly available the very full and up-to-date information scattered throughout the volume.

The vegetable fats themselves are considered under the usual headings of non-drying, semi-drying and drying oils, the individual materials being arranged mainly in alphabetical order of their common names, although here and there allied groups of fats, such as the chaulmoogra group, the kernel fats of the Palmae, or the Cruciferous seed-fats, are taken together. One wonders whether it is not almost time, in works of this kind, to classify the fats according to their major component acids. If this were done, it would be found, for the most part, that fats with similar applications, would fall together, and also in fairly close alignment with the botanical families from which they originate; whilst it would then be relatively simple, in each group, to consider first the technically important members, and then the less common, but often potentially interesting, ones.

Readers of THE ANALYST will probably be particularly interested in Chapter VI ("Methods"). On the whole, the procedures selected for full description are in accordance with the best standard practice, although possibly more alternatives might have been given, with advantage, in some of the routine methods (such as those for saponification and iodine value, or unsaponifiable matter), in order to cover the entire range of materials which demand consideration. Specific tests (which, of course, abound in this subject) are quoted at length, both in the chapter in question and in earlier parts of the book, under the headings of particular oils; here, again, however, the indexing should be made commensurate with the fullness and accuracy of the matter in the text. Before leaving the critical side of this notice, one must also regret the many lapses of the printer which have been condoned; in most cases they are insignificant and merely annoying, but in some instances might lead to serious misconstruction. Perfect proof-reading of so large a mass of data is admittedly difficult, but without it the value of a book of this kind is apt to be depreciated.

Printer's errors and the adequacy of indexes are, though important, but the mechanical side of book production, and they are given prominence here because this work deserves the best of all the necessary aids to its utilisation. On the other hand, one should acknowledge the very full bibliographical references which are given in the text, not only to original papers in the literature, but also to monographs and articles wherein different aspects of the subject are treated even more fully than in the book itself. The book is written in the light of the most recent work on all the matters dealt with, and is especially helpful because existing information has throughout been considered critically. Dr. Jamieson has not hesitated to point out when, in his opinion, alleged facts require further confirmation before acceptance, and, perhaps most welcome of all, he has ruthlessly eliminated a number of old, familiar statements which have been permitted far too long a residence in the permanent literature of the vegetable fats. The reviewer has rarely had the pleasure of reading such an interestingly presented and exhaustive account of the subject. T. P. HILDITCH.

POTENTIOMETRIC TITRATIONS. A THEORETICAL AND PRACTICAL TREATISE. By I. M. KOLTHOFF and N. H. FURMAN. Second Edition. Pp. 482. London: Chapman & Hall. 1931. Price 36s.

The rapid growth of the subject of potentiometric titrations is exemplified by the fact that, in the second edition of the book at present under review, over thirty-four pages are occupied by references to the literature, whereas, in the previous edition (see ANALYST, 1927, 52, 253), only sixteen pages were required.

The book has been extended by 137 pages, although the theoretical introduction has been reduced by 60 pages; thus it is evident that there has been a marked increase, during the past three or four years, in the practical applications of potentiometric titrations. A new and thoroughly up-to-date edition of this excellent book is, therefore, very welcome.

In order to permit the introduction of such a large amount of new material, the authors have been compelled, by the necessity of keeping the volume within reasonable bounds, to omit the first three chapters of the first edition. These chapters dealt with the principles of precipitation, neutralisation and oxidation-reduction reactions, and with electrode potentials and equilibrium constants; in their place has been written a short general introduction to the whole subject of electrometric titrations. This procedure has been justified on the grounds that the same material is adequately discussed in Kolthoff's *Volumetric Analysis*, Vol. I (ANALYST, 1929, **54**, 194), to which the reader is referred. The omission of a large portion of theory means that the book is no longer a complete treatment of electrometric titration, but, in view of the already imposing size of the book and its high price, it is just as well that the theoretical aspects, which can be obtained elsewhere, have been curtailed in favour of the practical information, which is otherwise only to be found distributed throughout a variety of scientific journals. Although a titration is essentially a practical process, it must be admitted that an understanding of the theory of the reaction being used is very desirable, and in this connection the book by Kolthoff and Furman will still prove satisfactory; although the general theory has been curtailed, the theory of each individual titration is given full treatment.

Of the topics dealt with in this new edition, two may be chosen for special mention, since they seem destined to play an important part in the future of the subject; these are the use of the thermionic (wireless) valve and the glass electrode. The treatment in both cases is very good, and references to the literature are given in full.

To those analysts who have already realised the advantages of potentiometric titration it is only necessary to state that the book under review is a very complete account of the subject; to those who have not yet seen the beauty of the electrometric method the book will prove a revelation. S. GLASSTONE.

APPLIED PHARMACOLOGY. By A. J. CLARK, M.C., M.D., F.R.C.P., F.R.S. Pp. x+590. 72 Illustrations. London: Fourth Edition. J. & A. Churchill. 1932. Price 17s.

Professor Clark's book, now a classic of pharmacology, appears in a welcome fourth edition. Two years only have elapsed since the third edition was published, a sign of the rapid progress now being made in "the study of the action of drugs on living tissues."

The chapters on the endocrine glands and on the vitamins themselves bear witness to this progress: they register an advance that is not always credited with its full significance. Hormones and accessory food factors have now ceased to be the monopoly of the physiologist and biochemist respectively; their use by the practising physician brings them into the great category of materia medica. It is daily becoming more probable that their action in the large doses that the chemist can provide and the pharmacologist assay, is so different in degree from their normal action in healthy metabolism as to be almost a difference in kind. Massive doses of adrenaline or insulin or vitamin *D* may, indeed, produce death, so that precise knowledge of their pharmacology is more than ever necessary.

Professor Clark devotes chapters to subjects as far removed as Disinfectants, Radiation, Immunity, and Respiration. Pharmacology is treated throughout in a way fully justifying the title of his book, with, that is to say, complete practicality. The book is divided into chapters that are, for the most part, based on the organ or organs affected by the drugs discussed—so that we have the pharmacology of the Central Nervous System (four chapters), of the Alimentary Canal (three chapters), of the Circulation (two chapters), and so on. Chapters on the specific therapeutic action of arsenic; mercury, bismuth, and antimony; quinine and emetine: on anthelminthics: and on inorganic metabolism, besides those already mentioned, constitute the bulk of the book, which has also a useful index of fifteen pages and an interesting introductory chapter.

In such a forest of information we may unearth strange and arresting facts by the simple process of browsing. Thus we learn that the rabbit's liver contains an enzyme that destroys atropine, thereby enabling the animal to eat belladonna leaves with impunity; that organic arsenicals must not be given to patients with visceral disease; that iodide prophylaxis may result in hyperthyroidism, so replacing one evil by another nearly as serious; that calcium should be given before using carbon tetrachloride medicinally, as it counteracts the tendency of the latter to produce liver injury; that water poisoning can be produced by the combined action of pituitary extract and water.

Criticisms, so slight as to be negligible, might be made of the statements that "the best methods of drying milk retain about one-half of the vitamin *C* content"; that vitamin *B* "occurs only in the germ of seeds" (what is meant is that in seeds it occurs in the germ only!); that ethyl chaulmoograte is a mixture of the fatty acids of chaulmoogra oil: to the use of C_H values instead of the now universally understood *p*H: to the omission of any discussion of Besredka's so-called "antivirus" phenomena: to the absence of any reference to the action of vitamin *D* on disorders of the peripheral circulation or to the effect of vitamin *B* deficiency on the heart. There are a few minor misprints, such as "acetyl chlorine" for "acetyl chloride" on line 2, page 575.

The lists of preparations given at the ends of chapters, with the approximate costs of the various drugs and galenicals, are particularly original features.

The book should prove highly interesting to many who, perhaps, have no professional use for it. It should prove valuable to all who come occasionally into technical contact with drugs and their effects. It will be indispensable to pharmaceutical chemists, toxicologists, pharmacologists, physiologists, and writers of detective fiction.

A. L. BACHARACH.

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, May 4th, the President, Mr. F. W. F. Arnaud, being in the chair.

Certificates were read for the first time in favour of Charles Carr Marginson, B.Sc., A.I.C., Ph.C., Wilfred Mather, A.M.C.T., F.I.C., Alec Duncan Mitchell, D.Sc., F.I.C., and M. Niyogi, M.Sc.

Certificates were read for the second time in favour of Reginald Haydn Hopkins, D.Sc., F.I.C., and William Basil Walker, B.Sc., A.I.C.

The following were elected Members of the Society:—Edward Bertram Anderson, M.Sc., F.I.C., Edward Foster Eaton, Frank Maudsley, B.Sc., F.I.C., Samuel Gordon Stevenson, B.Sc., B.Pharm., F.I.C., and James William Thom, B.Sc.

The following papers were read and discussed:—"The Quantitative Separation of Tantalum, Niobium, Titanium and Zirconium, and a New Analytical Grouping," by W. R. Schoeller, Ph.D., and A. R. Powell (*Work done under the Analytical Investigation Scheme*); "The Iodine and Thiocyanogen Values of Irish Butter," by P. S. Arup, M.Sc., F.I.C.; "Sediments in Ink and in Writing," by C. Ainsworth Mitchell, D.Sc., F.I.C., and T. J. Ward; and "The Determination of Minute Amounts of Copper in the Presence of Iron and certain other Metals," by L. G. Haddock, B.Sc., and Norman Evers, B.Sc., F.I.C.

Death

With great regret we record the death, on May 23rd, of Dr. J. C. Thresh. An obituary notice will be published later.

Phloroglucinol Method for the Determination of Mechanical Wood Pulp in Paper

By H. B. DUNNICLIFF, M.A., Sc.D., F.I.C., and H. D. SURI, M.Sc.

(*Read at the Meeting, February* 3, 1932)

The determination of mechanical wood pulp (M.W.P.) in cheap newsprint has been attempted by various physical (optical) and chemical methods. Of the latter, the volumetric phloroglucinol method of Cross and Bevan (*Papier Ztg.*, 1907, **32**, 4113, 4479) is the most accurate quantitative method proposed. The details of this may be found in standard analytical text-books [*cf. Allen's Commercial Organic Analysis*, Vol. I (1923), p. 626].

In India this method did not give reliable results, and we have attempted to find (*a*) the effect of temperature on the result; (*b*) the relationship between the volume of standard reagent and the weight of paper necessary for quantitative action; (*c*) the time required for quantitative action; and (*d*) the mechanism of the reaction.

The formula of Cross and Bevan for the calculation of the percentage, H, of M.W.P. in paper depends upon the terms, x, y and z in the equation:

$$H = \frac{100\,(x - y)}{z - y} \quad \ldots\ldots\ldots\ldots \quad (1)$$

in which y, z and x are the weights of crystalline phloroglucinol required to react with 100 grms. of chemical pulp, mechanical wood pulp and pulp in the samples under examination, respectively.

As a result of many experiments, Cross and Bevan gave $y = 1$ and $z = 8$ as average values for these terms, though other workers have proposed figures which differ more or less widely from them.

In India, where high temperatures are ordinarily prevalent, reliable results cannot be guaranteed if a hydrated compound which has an appreciable vapour pressure is adopted as the weighed fundamental criterion. For this reason, in the work to be described, anhydrous phloroglucinol, obtained by heating the hydrated compound at 110° C., was used throughout. That the dehydrated compound does not undergo any constitutional change in the drying process (other than the loss of water) was shown by the fact that equal volumes of equivalent solutions of hydrated and dehydrated phloroglucinol required the same quantity of standard formaldehyde solution for complete interaction, as represented by the equation:

$$2C_6H_3(OH)_3 + HCHO = CH_2:(C_6H_2(OH)_3)_2 + H_2O \quad \ldots\ldots\ldots\ldots \quad (2)$$

Accepting the form of Cross and Bevan's equation and writing it

$$H = \frac{100\,(x - a)}{\beta - a} \quad \ldots\ldots\ldots\ldots \quad (3)$$

in which α, β and x are the weights of anhydrous phloroglucinol required to react with 100 grms. of chemical pulp, mechanical wood pulp, and pulp in the unknown sample, respectively, the values of α and β had to be determined.

"ABSORPTION VALUE."—Throughout this report the amount of phloroglucinol removed from the solution by a paper or pulp is referred to as the amount "absorbed." As shown in the sequel, this includes phloroglucinol removed both by chemical action and by adsorption. The "absorption value" is the number of grms. of anhydrous phloroglucinol absorbed by 100 grms. of dry ash-free paper or pulp.

TIME.—As regards the time required for quantitative reaction, it may be stated that the reaction is found to be complete after 12 hours at 35° C., the standard temperature decided upon for the operation (*vide* p. 356). Since, however, working conditions made this period rather awkward, the time proposed by Cross and Bevan, *i.e.* 18 hours, was uniformly adopted. Bottles were usually placed in the bath at 5 p.m. and removed at 11 a.m. next day.

DETERMINATION OF THE ABSORPTION FACTORS.—A constant amount (1 grm.) of each kind of dried pulp was treated with varying quantities of 0·5 per cent. anhydrous phloroglucinol in hydrochloric acid (12 per cent.) for equal periods of time. Flasks containing the reaction mixture were rotated under water in an electrically regulated thermostat capable of being controlled to ± 0·1° C.

For these experiments, formaldehyde solution was made up as prescribed by Cross and Bevan (*loc. cit.*), and the titration was carried out as formulated by them. The determination of the end-point (cheap newsprint being used as indicator) was carried out in the last stages by "triple spotting," *i.e.* putting a drop three times on the same spot on the paper and drying after the placing of each drop, as described by Cross and Bevan.

TABLE I

ABSORPTION FACTORS

Showing the effect of the quantity of anhydrous phloroglucinol and of temperature on the absorption values of Amsterdam pulps.

A. *Chemical Pulp* (*S.P.*)

Volume of solution per grm. of pulp c.c.	At 20° C.	At 25° C.	At 30° C.	At 35° C.
20	0·79	0·90	1·04	1·14
30	0·84	1·03	1·17	1·16
40	0·86	1·13	1·16	1·21
50	0·90	1·21	1·18	1·22
100	0·91	1·20	1·21	1·21
	B. *Mechanical Wood Pulp* (*M.W.P.*)			
20	5·26	6·27	6·45	7·09
30	5·61	6·70	6·95	7·86
40	6·12	7·20	7·43	8·51
50	6·65	7·22	7·65	8·52
100	7·34	7·43	7·67	8·60
150	7·40	—	—	—
200	7·30	—	—	—

These figures show (1) that the absorption values of S.P. and M.W.P. for 0·5 per cent. (anhydrous) phloroglucinol solution increase with the increase of the volume of phloroglucinol solution used to react with a constant weight of pure pulp in each case, and (2) that at different temperatures different maximum absorption values are obtained. These are realised at 25°, 30° and 35° C. if 1 grm. of paper is treated with 50 c.c. of the phloroglucinol solution. At 20° C. a much greater volume of this reagent is required for complete reaction.

Hence, the original method, in which 2 grms. of paper or pulp are used with 40 c.c. of 0·5 per cent. crystalline phloroglucinol solution (=0·389 per cent. anhydrous phloroglucinol), at ordinary European temperatures would fail to effect the maximum absorption which the successful operation of this method demands. We find that the factors of Cross and Bevan are valid, and give good results with mixtures of a limited range of composition and at low temperatures, but that they are not valid for wide ranges of composition or temperature, or for the fixed high temperature which it is necessary for the analyst in India to employ for the sake of uniformity at different places.

It is imperative, therefore, that analyses should be made under carefully specified conditions. These require that (1) a fixed amount of paper should be treated with (2) a fixed volume of standard phloroglucinol solution, which shall be (3) sufficient to give maximum absorption (4) at a particular temperature, and (5) for a definite period of reaction. These factors should also be independent of the percentage of mechanical wood pulp present in the paper.

RESULTS WITH ARTIFICIAL MIXTURES.—To illustrate the above statement, artificial mixtures of the two pulps were exposed to the action of 100 c.c. of phloroglucinol solution at 20° C. (to give maximum absorption), and the results in Table II were obtained.

TABLE II

TEMPERATURE 20° C.

M.W.P. in mixture Per Cent.	Absorption value	M.W.P. (calc.). Constants (*vide* Table I) $\alpha=0{\cdot}91$ and $\beta=7{\cdot}34$ Per Cent.
80	6·10	80·7
60	4·86	61·4

An error of 1 to 1·5 per cent. would be accounted for by a difference of one drop (0·05 c.c.) of formaldehyde in the titration reading. The time required to titrate volumes of solutions greater than the 10 c.c. ordinarily used was excessive.

It is essential, therefore, that determinations should be carried out at a temperature easily attainable at all seasons, and that a concentration of phloroglucinol should be adopted which would give a maximum absorption at that temperature. The temperature finally selected was 35° C., although that is occasionally lower than laboratory temperature (temperatures up to 40° C. have been recorded), and the absorption values of S.P. and M.W.P. from different sources were determined when 1 grm. of the pulp was exposed to the action of 50 c.c. of 0·5 per cent. anhydrous phloroglucinol solution (*vide* Table III).

TABLE III

ABSORPTION FACTORS OF PHLOROGLUCINOL AT 35° C.

	Quality.	S.P.	M.W.P.
1.	Amsterdam	1·26	8·54
2.	Norwegian	1·10	8·68
	,, (paper form)	—	8·48
3.	Boregard	—	8·72
4.	Finska	—	8·48
5.	Swedish	1·20	—
		Mean=1·187	Mean=8·57

ABSORPTION VALUES OF PULPS AND PAPER OF KNOWN COMPOSITION.—Table IV gives the absorption values and compositions of certain pulps and specially made standard papers of known composition, together with the calculated composition, the absorption values shown in Table I being used for 50 c.c. of solution to 1 grm. of pulp at various temperatures. In these cases the ash was negligible.

TABLE IV

ABSORPTION OF ANHYDROUS PHLOROGLUCINOL BY STANDARD PAPERS AND KNOWN MIXTURES (A.M.) AT VARIOUS TEMPERATURES

	Composition of standard paper and artificial mixtures		25° C.		30° C.		35° C.	
	M.W.P. Per cent.	S.P. Per cent.	Absorption per 100 grms. of paper	Calc. per cent. of M.W.P. consts. $\alpha=1{\cdot}21$ $\beta=7{\cdot}22$	Absorption per 100 grms. of paper	Calc. per cent. of M.W.P. consts. $\alpha=1{\cdot}18$ $\beta=7{\cdot}65$	Absorption per 100 grms. of paper	Calc. per cent. of M.W.P. consts. $\alpha=1{\cdot}22$ $\beta=1{\cdot}52$
A.M.	80	20	—	—	—	—	7·02	79·5
Paper	75	25	—	—	—	—	6·78	76·1
,,	70	30	5·38	69·4	5·82	71·7	6·39	70·8
,,	60	40	4·69	58·0	5·13	61·1	5·38	59·7
,,	50	50	4·18	49·5	4·41	49·9	4·85	49·7
A.M.	40	60	—	—	—	—	4·20	40·8

STUDY OF THE MECHANISM OF THE REACTION BETWEEN MECHANICAL WOOD PULP AND PHLOROGLUCINOL AT 35° C.—One grm. of the mechanical wood pulp was exposed in a series of stoppered bottles to the action of the same volume of phloroglucinol solution of different concentrations in a thermostat at 35° C. for 18 hours. The contents were then filtered and titrated against formaldehyde as before. The results are given in Table V.

TABLE V

	Amount of Phloroglucinol		
	In 50 c.c. of original solution Mgrms.	Absorbed by 1 grm. of M.W.P. = C_s Mgrms.	Remaining in 50 c.c. of solution after equilibrium = C_e Mgrms.
1.	25·0	20·0	5·0
2.	50·0	40·0	10·0
3.	75·0	50·8	24·2
4.	100·0	60·0	40·0
5.	112·5	64·5	48·0
6.	125·0	67·8	57·2
7.	137·5	71·0	66·5
8.	150·0	73·5	76·5
9.	162·5	75·0	87·5
10.	175·0	77·0	98·0
11.	187·5	78·4	109·1
12.	200·0	80·0	120·0
13.	212·5	81·8	130·7
14.	225·0	83·2	141·8
15.	237·5	85·4	152·1
16.	250·0	87·2	162·8

The curve obtained by plotting C_e against C_s resembles a typical adsorption isotherm, which is usually represented by the relationship:

$$C_s = K \times C_e^{\frac{1}{p}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$\text{or} \quad \log C_s = \frac{1}{p} \log C_e + \text{constant} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The values of the constants in (4) in this case are $K = 4{\cdot}40$ and $p = 4{\cdot}15$.

Hence, if log C_e is plotted against log C_s, a straight line should result, and, with the exception of No. 1, this is the case with the values given in Table V. Since the value for No. 1 does not fall on the straight line, it appears that the results are affected by some other influence. This may be due to a chemical action which takes place predominantly in the early stages of the action between the lignin of the mechanical wood pulp and the phloroglucinol.

The extent to which chemical action takes place was shown by exposing 1 grm. of M.W.P. to 50 c.c. of 0·5 per cent. of phloroglucinol solution for 20 hours at 35° C. The pulp (which had taken up 0·0870 grm. of phloroglucinol) was then repeatedly extracted with 12 per cent. hydrochloric acid (sp.gr. 1·06) at 35° C., until the extracts showed negligible tests for phloroglucinol.

Determinations of the phloroglucinol in the collected extracts showed that 0·0677 grm. of the phloroglucinol was not removable from the solid phase, *i.e.* it had presumably entered into chemical combination with the lignin of the M.W.P. Thus, in addition to the 0·0677 grm. of phloroglucinol which takes part in the chemical reaction, 0·0193 grm. of phloroglucinol is retained by each gram of M.W.P. in some physical condition.

THE VELOCITY OF THE REACTION.—An attempt was made to determine the velocity at which the chemical reaction proceeds and the order of the reaction. A number of bottles, each containing 1 grm. of M.W.P. and 50 c.c. of phloroglucinol solution, were rotated in a thermostat at 35° C., and the reaction was stopped after definite intervals of time. The results are shown in Table VI.

TABLE VI

SHOWING THE AMOUNT OF PHLOROGLUCINOL WHICH HAD REACTED WITH 100 GRMS. OF M.W.P. AFTER THE INTERVALS OF TIME SHOWN IN COLUMN ii

Total amount of phloroglucinol available = 25 grms.

i	ii	iii	iv	v	
No.	Time in hours	Phloroglucinol removed from the solution in grms.	$\frac{1}{t}\log\frac{a}{a-x}=\mathrm{K}$	$\frac{1}{t+2{\cdot}3}\log\frac{a}{a-x}=\mathrm{K}_1$	
	$=t$	$=x$	$a=25$	$a=25$	
1.	0·25	4·372	0·3336	0·0327	
2.	0·50	4·950	0·1916	0·0342	
3.	0·75	5·166	0·1340	0·0329	Mean= 0·0328
4.	1·00	5·279	0·1030	0·0312	
5.	1·50	6·270	0·0836	0·0330	
6.	2·00	6·518	0·0656	0·0305	
7.	2·50	6·766	0·0545	0·0285	
8.	3·00	7·096	0·0484	0·0273	
9.	4·00	7·474	0·0386	0·0245	

The high initial value of x shows that there is a very rapid reaction at first which it is not possible to measure. Assuming that the reaction is unimolecular (or bimolecular), we can determine the time, t_1, which the amount of change represented by the initial rapid action would have taken if the reaction had proceeded with a normal velocity from the start.

The method of calculation is shown in detail by Dunnicliff and Butler (*J. Chem. Soc.*, 1921, **119**, 1384) for a homogeneous system, and, for a heterogeneous system, by Dunnicliff, Suri and Malhotra (*J. Chem. Soc.*, 1928, 3106). The value of t_1 has been determined by equating pairs of expressions

$$\frac{1}{t+t_1}\log\frac{a}{a-x}$$

for various values of t and x from data shown in Table VI, experiments (1) to (5).

The mean of six such calculations gave $t_1 = 2{\cdot}3$ hours. The values found for the constant, K_1, for a unimolecular reaction are recorded in column v of Table VI, and show a reasonable constancy round the mean value $\mathrm{K}_1 = 0{\cdot}0328$. Calculation as for a bimolecular reaction does not give a more constant value for K or K_1. These results indicate that for a period of about 1·5 hours (corrected time including the abnormal period = 3·8 hours) the reaction is unimolecular.

The velocity of the reaction then slows down until, after about 8 or 9 hours (actual time), it is nearly negligible.

The curve found by plotting C_e against C_s (Table V) is indicative of adsorption, and the conclusion one must deduce from the two sets of results is that adsorption precedes chemical action (which is most rapid at first), and that there is some definite relationship between the chemical action and adsorption phenomena. This is borne out by the fact that, although much of the adsorbed phloroglucinol enters into irreversible chemical combination with a component of the M.W.P., the form of the curve remains unchanged.

Since the reaction involves both chemical action and adsorption proceeding side by side, it is clear that the only prospect of obtaining satisfactory results in the determination of M.W.P. in paper by this reaction depends upon having conditions clearly defined as set forth on p. 356. It is also essential that sufficient excess of reagent should be used to supply adequate phloroglucinol for the balanced system (represented by chemical combination and adsorption) to be in equilibrium with the solution left after giving the necessary amount of phloroglucinol to that system. These conditions must be realisable for papers containing widely different percentages of M.W.P.

We and other chemists in this laboratory have analysed several hundreds of samples of paper, both commercial varieties and papers specially made as standards, and have found that, for the papers of known composition, the following procedure gives results accurate to about 1 per cent.

DETERMINATION OF MECHANICAL WOOD PULP IN PAPER.—About 6 to 8 grms. of paper are cut from different parts of the sheet or sheets under examination. These are rolled into a packet and suspended by a thread beneath a reflux condenser inside a conical flask containing 50 c.c. of 90 per cent. alcohol. The flask is then heated on a water-bath for 2–3 hours, or, with coloured paper until as much as possible of the colour is removed. This treatment also removes a portion of the sizing materials. The paper is now drained, cut into small pieces (about 3–4 mm. square) and dried to constant weight at 100° C.

Correction for Mineral Loading.—Since the percentage of M.W.P. on the fibre content of the paper is usually required, the percentage of loading material in the paper must be determined and a correction applied. For this purpose, about 2 grms. of the dried paper are "ashed," and the amount of the incombustible and non-volatile residue is accepted as a measure of the mineral loading material present.

Determination of "Absorption Value."—To determine the "absorption value," 1 grm. of the dried paper is placed in a clean, dry, glass-stoppered 4-ounce bottle; 50 c.c. of the standard phloroglucinol solution (0·5 per cent.) are added from a pipette, and the bottle is sealed with wax. After being shaken several times to cause the pieces of paper to sink to the bottom, the bottle is placed in a thermostat at 35° C. (±0·1° C.) for 18 hours. The contents of the bottle are rapidly filtered through a cotton-wool plug into another clean dry bottle, supported in the thermostat at the same temperature. The solution is then cooled to room temperature, 10 c.c. are measured into a conical flask, 20 c.c. of hydrochloric acid

(12 per cent., sp.gr. 1·06) are added, and the titration is carried out as described by Cross and Bevan. As a control, 10 c.c. of the standard phloroglucinol solution are then titrated under identical conditions. The difference between the volume of formaldehyde solution required for the control and the volume required for the solution which has reacted with the paper, multiplied by 5, is a measure of the phloroglucinol which has been taken up by 1 grm. of the paper. From this the weight of phloroglucinol is determined in grms. and, when multiplied by 100, this gives the value of x in the equation:

$$H = \frac{100 \times \left(\frac{100x}{100\text{—per cent. of ash}} - 1{\cdot}20\right)}{8{\cdot}56 - 1{\cdot}20} \quad\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

$$\text{or} \quad H = 13{\cdot}587 \times \left(\frac{100x}{100\text{—per cent. of ash}} - 1{\cdot}20\right) \ldots\ldots\ldots\ldots\ldots \quad (7)$$

In the determination of M.W.P. in commercial papers a blank test was always carried out on a standard paper of approximately the same M.W.P. content, as determined by the Spence and Krauss optical method. A correction may be applied to compensate for the possible error referred to on p. 360.

We wish to acknowledge the assistance of the late Lala Kishen Lal, M.Sc., who did useful work in the early stages of this investigation by analysing many samples, and of Lala Kishen Prasad, M.Sc., who also carried out a number of analyses and commenced an investigation on the influence of fillers, sizing and dyes on the validity of the method. The results of that investigation are not yet sufficiently definite for inclusion in this paper.

Funds for this investigation were provided by the Central Board of Revenue, and this paper is published with the permission of the Government of India.

CENTRAL BOARD OF REVENUE,
CONTROL LABORATORY, LAHORE, INDIA.

Some Analytical Applications of Sodium Hydrosulphite. II*

Separation of Tin from Copper, Zinc, Lead, etc., and from Oxalic Acid Determination of Tin in Steel

By B. S. EVANS, M.C., Ph.D., F.I.C.

(*Read at the Meeting, February* 3, 1932)

It was shown in the first part of this paper (Analyst, 1929, **54**, 395) that certain metals, *e.g.* antimony, lead and bismuth, could be precipitated as metal from a hot alkaline cyanide solution by treatment with sodium hydrosulphite and thus be separated quantitatively from, *e.g.* copper. Tin under these conditions does not precipitate as metal; if, however, an excess of ammonium salts is present, ensuring the absence of alkali other than ammonia, a chocolate brown precipitate, apparently stannous sulphide, is thrown down on boiling; this reaction, which is only partial, seems to depend on the formation of sulphide, owing to the break-up of the sodium hydrosulphite molecule; it will be remembered that cadmium under the same conditions may be deposited partly or entirely as yellow cadmium sulphide. If ammonium sulphide is added to the solution before the hydrosulphite, the reaction proceeds to completion, and, since stannous sulphide is quite insoluble in ammonia or ammonium sulphide, and the precipitate is very dense and powdery, it forms a clean and rapid method of separating tin from various metals whose sulphides are soluble in alkali cyanide, and which are not precipitated as metal by hydrosulphite under these conditions, notably copper, iron, nickel, and zinc.

Process.—In the absence of large amounts of interfering metals (*e.g.* copper, lead, zinc, etc.), the solution containing the tin is treated with excess (say 10 c.c.) of citric acid solution (100 grms. dissolved in 200 c.c. of water), and made alkaline with ammonia; 10 c.c. of potassium cyanide solution (saturated), 25 c.c. of ammonium chloride solution (20 per cent.) and 10 c.c. of ammonium sulphide are then added, followed by about 7 grms. of sodium hydrosulphite, and the solution is boiled for one minute; at the end of this time it is allowed to stand for a minute or so to let the temperature drop just below boiling point, 2 or 3 grms. more of sodium hydrosulphite are added, and the flask is allowed to stand for about 15 minutes on the steam-bath. The liquid is next filtered, hot, through a closely-packed pulp filter, the precipitate is washed, with as little delay as possible, four times with an almost boiling 5 per cent. solution of ammonium chloride, containing 10 c.c. of potassium cyanide solution (saturated) and 2 or 3 grms. of sodium hydrosulphite per 200 c.c. (this treatment is to remove any traces of copper, zinc, iron, etc., which may be present), and then three times with hot 5 per cent. ammonium chloride solution.

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* Communication from the Research Department, Woolwich.

The precipitate now contains all the tin, all the lead and bismuth and most of the antimony contained in the original solution, none of which metals in moderation interfere with the final determination of the tin, but it is free from copper, nickel, iron, zinc, etc., some of which interfere very seriously with the volumetric determination. The pulp (with the precipitate) is shaken into a beaker and treated with a mixture of 10 c.c. of sodium hydroxide solution (20 per cent.) and 20 c.c. of hydrogen peroxide, which is used to rinse down the sides of the funnel and beaker; the pulp is thoroughly broken up with a glass rod, the liquid is heated nearly to boiling, and, after the addition of 30 c.c. of citric acid solution (100 grms. in 200 c.c. of water), it is boiled for a few moments; the solution is next filtered from the pulp through a very small pulp filter into a beaker, and the pulp is pressed down with the glass rod and thoroughly washed with hot water.

The filtrate is evaporated to about 25 c.c., cooled, poured into a measuring cylinder, and roughly measured; it is then poured into a 750-c.c. conical flask and rinsed in with an approximately equal volume of strong hydrochloric acid, and the beaker and measuring cylinder are finally rinsed in with repeated quantities of dilute (1:1) hydrochloric acid, sufficient in all to bring the total volume in the flask up to about 100 c.c.; about 4 grms. of sodium hypophosphite and 1 c.c. of saturated mercuric chloride solution are added, and the mouth of the flask is closed with the attachment for tin titrations described in former papers (Evans, ANALYST, 1927, **52**, 570; 1931, **56**, 172). The flask is swept out with a rapid stream of carbon dioxide for ten minutes, the liquid is then boiled with carbon dioxide passing for a further 15 minutes, after which it is cooled, diluted and titrated exactly as described (ANALYST, 1931, **56**, 173), the only difference being that no citric acid is added to the diluting water. Trials of the above process with known amounts of tin in the absence of other metals, gave the following results:

Tin taken Grm.	Titration *N*/10 iodine solution c.c.	Tin found Grm.
0·0500	8·40	0·0498
0·0400	6·70	0·0398
0·0300	5·15	0·0306
0·0200	3·35	0·0199
0·0100	1·70	0·0101

SEPARATION FROM LARGE AMOUNTS OF COPPER (*e.g.* DETERMINATION OF TIN IN BRONZE).—The procedure adopted was as follows:—Five grms. of the sample were dissolved in 50 c.c. of dilute nitric acid (sp.gr. 1·2) and 10 c.c. of strong hydrochloric acid, 20 c.c. of the citric acid solution were added and, after making the liquid alkaline with ammonia, the blue colour was just discharged with the potassium cyanide, and 10 c.c. of the latter were added in excess; the ammonium sulphide and sodium hydrosulphite were then added, and the remainder of the process was carried out as before. Results:

Copper taken Grms.	Tin taken Grm.	Titration c.c.	Tin found Grm.	Tin added Per Cent.	Tin found Per Cent.
5·00	*Blank	0·5 (*N*/100)	0·0003	—	—
5·00	0·0500	8·50—0·05 (*N*/10)	0·0502	1·00	1·00
5·00	0·0400	6·65—0·05 (*N*/10)	0·0392	0·80	0·78
5·00	0·0300	5·05—0·05 (*N*/10)	0·0297	0·60	0·59
5·00	0·0200	3·40—0·05 (*N*/10)	0·0199	0·40	0·40
5·00	0·0100	1·65—0·05 (*N*/10)	0·0095	0·20	0·19
5·00	0·0050	8·8 —0·5 (*N*/100)	0·0049	0·100	0·098
5·00	0·0040	6·9 —0·5 (*N*/100)	0·0038	0·080	0·076
5·00	0·0030	5·4 —0·5 (*N*/100)	0·0029	0·060	0·058
5·00	0·0020	3·9 —0·5 (*N*/100)	0·0020	0·040	0·040
5·00	0·0010	2·0 —0·5 (*N*/100)	0·0009	0·020	0·018

SEPARATION FROM LARGE AMOUNTS OF COPPER AND ZINC (DETERMINATION OF TIN IN BRASS).—In this case the procedure was almost the same, but, on the addition of ammonium sulphide, after decolorisation of the copper, zinc sulphide precipitated; potassium cyanide solution was then added until the zinc sulphide had redissolved, followed by 20 c.c. in excess, an excess of ammonium chloride was added (about 20 grms.), followed by the hydrosulphite, the liquid was boiled, and the determination was finished as before. Results obtained were as follows:

Brass taken Grms.	Tin added Grm.	Titration c.c.	Tin found Grm.	Tin added Per Cent.	Tin found Per Cent.
5·0	*Blank	0·8 (*N*/100)	—	—	—
5·0	0·050	8·50—0·10 (*N*/10)	0·0499	1·00	1·00
5·0	0·100	17·00—0·10 (*N*/10)	0·1003	2·00	2·01
5·0	0·030	5·05—0·10 (*N*/10)	0·0294	0·60	0·59
5·0	0·010	1·75—0·10 (*N*/10)	0·0098	0·20	0·20
5·0	0·0050	9·1 —0·8 (*N*/100)	0·0049	0·100	0·098
5·0	0·0030	5·6 —0·8 (*N*/100)	0·0028	0·060	0·056
5·0	0·0020	3·9 —0·8 (*N*/100)	0·0018	0·040	0·036
5·0	0·0010	2·2 —0·8 (*N*/100)	0·0008	0·020	0·016

* The blank in these two cases represents tin present in the metals used; accordingly, 0·5 c.c. of *N*/100 and 0·05 c.c. of *N*/10 solutions, in the case of copper, and 0·8 c.c. of *N*/100 and 0·10 c.c. of *N*/10 solutions, in the case of brass, has been deducted from the titration figure.

The case of the determination of tin in brass brings out a point which it is important to bear in mind. Stannous sulphide, whilst insoluble in ammonia and in alkali hydroxides, is apparently not produced by hydrosulphite reduction in presence of the latter, and potassium cyanide is strongly alkaline; it is, therefore, essential that an excess of ammonium salts should be present to eliminate the retarding power of the potassium cyanide used. In the case of copper this excess is furnished by the acid used in dissolving the sample, which is subsequently neutralised with ammonia; in the case of brass, the ammonium salts thus present are not sufficient, owing to the large excess of cyanide which has to be used, and consequently it was found necessary to add not less than 20 grms. of ammonium chloride. It is always desirable to test the filtrate and washings to ensure complete precipitation; to do this, they are boiled with the addition of a little more hydrosulphite, but in case the ammonium salts have been insufficient, more ammonium chloride should be added as well. It sometimes happens that the decomposition of cyanide caused by boiling with ammonium salts brings the amount present below that required to keep the copper sulphide in solution; therefore, before assuming that a darkening appearing when the filtrate is tested is due to incomplete precipitation, it is well to add a few drops of the cyanide solution, which will redissolve any copper sulphide thus formed, while leaving stannous sulphide untouched.

SEPARATION FROM LEAD.—Attempts were made to separate tin from lead and antimony by this method. The precipitation of lead as metal by hydrosulphite will apparently take place equally well in sodium hydroxide solutions, whilst that of stannous sulphide is inhibited by this reagent. Accordingly, 5-grm. quantities of lead, to which varying amounts of tin had been added, were dissolved in 50 c.c. of citric acid solution (100 grms. dissolved in 200 c.c. of water) and 50 c.c. of dilute nitric acid (sp.gr. 1·2), sodium hydroxide solution (20 per cent.) was added until the precipitate first formed redissolved, then 10 c.c. of saturated potassium cyanide solution (treated with 2 or 3 drops of bromine water), and, finally, sodium hydroxide solution again until the precipitate redissolved, and then 10 c.c. in excess; about 7 grms. of hydrosulphite were added, and the liquid was heated to boiling; it was then cooled and filtered, and the precipitated lead was washed with a mixture of 10 c.c. of saturated potassium cyanide solution, 10 c.c. of sodium hydroxide solution (20 per cent.), 5 grms. of sodium chloride and 2 grms. of sodium hydrosulphite in 200 c.c. To the filtrate were added 20 grms. of ammonium chloride, 5 grms. of hydrosulphite and 10 c.c. of ammonium sulphide; it was heated to boiling, and the tin was determined as before. The following results were obtained:

Lead taken Grms.	Tin added Grm.	Titration c.c.	Tin found Grm.	Tin added Per Cent.	Tin found Per Cent.
5·0	0·1000	16·72 (*N*/10)	0·0993	2·00	1·99
5·0	0·0700	11·63 (*N*/10)	0·0691	1·40	1·38
5·0	0·0500	8·26 (*N*/10)	0·0491	1·00	0·98
5·0	0·0200	3·27 (*N*/10)	0·0195	0·40	0·39
5·0	0·0100	1·71 (*N*/10)	0·0101	0·20	0·20

The precipitated lead in each case was tested for tin, with negative results. The above figures seem to show that the method gives a very fair separation of tin from lead.

ATTEMPTED SEPARATION FROM ANTIMONY.—The method used for lead was tried for antimony, but with indifferent success. Only 0·1 grm. of antimony was taken, and varying amounts of tin were added, but the separation was by no means complete, as not only were traces of tin found in the antimony, but antimony was also found in the stannous sulphide precipitate. The figures obtained for the tin were, however, only slightly low. Results were as follows:

Antimony taken Grm.	Tin added Grm.	Titration c.c.	Tin found Grm.
0·10	0·1000	16·66 ($N/10$)	0·0989
0·10	0·0700	11·63 ($N/10$)	0·0691
0·10	0·0500	8·21 ($N/10$)	0·0488
0·10	0·0200	3·03 ($N/10$)	0·0180
0·10	0·0100	1·61 ($N/10$)	0·0096

SEPARATION OF TIN FROM IRON.—Experiments showed that there is no difficulty in separating tin from large amounts of iron, the iron being first quantitatively converted into ferrocyanide by the action of potassium cyanide and hydrosulphite. The amount of cyanide required, however, is so large that, in view of easy separations by other means, the method did not seem worth following up. In addition to this, the presence of another metal having a ferrocyanide sparingly soluble in alkaline solution (*e.g.* manganese) might cause serious complications.

DETERMINATION OF TIN IN STEEL.—The above considerations made it seem desirable to effect an initial separation from the iron present by means of hydrogen sulphide; trials made on these lines, however, gave very low results, and it soon became apparent that the tin was not being completely precipitated.* Attempts were, therefore, made by the addition of a relatively large amount of another precipitable metal (*e.g.* copper) to obtain complete precipitation; the results obtained, whilst occasionally correct, were generally low; it would seem that tin does not co-precipitate with copper to any large extent. Analogy of the two metals and the difficulty experienced in separating them led to the trial of antimony as co-precipitant, and this gave satisfactory results. Bearing in mind the fact that nearly all steels contain traces of copper, and that the latter metal has a very bad influence on the volumetric determination of tin, the tin was subsequently precipitated as stannous sulphide as described further back; this, of course, involved the precipitation of, at least, the greater part of the antimony, but as shown in a previous paper (Evans, ANALYST, 1931, **56**, 174), antimony in reasonable amount need have no harmful influence on the titration.

Process.—The steel used for these experiments had the following composition: —Carbon, 0·29; silicon, 0·025; manganese, 0·25; nickel, 2·05; and chromium, 2·20 per cent. Samples were dissolved in dilute (1:6) sulphuric acid (for 5 grms. 100 c.c. were used). Varying amounts of tin in solution were added, followed in each case by 0·05 grm. of antimony in solution in dilute (1:1) hydrochloric acid. The mixture was diluted with an equal volume of water, hydrogen sulphide was passed for about 15 minutes, and the flask was allowed to stand for 30 minutes. After this time the precipitated sulphides were filtered off and washed with

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* Scherrer (*Bur. of Standards., J. Research*, 1932, **8**, 309) finds the same difficulty where (as above) the hydrogen sulphide is passed into the *ferrous* solution; he avoids it by oxidising all the iron to the ferric state with nitric acid; this involves large amounts of sulphur being precipitated along with the sulphides.

5 per cent. ammonium chloride solution; the funnel having been transferred to the original flask, a mixture of 10 c.c. of sodium hydroxide solution (20 per cent.) and 10 c.c. of hydrogen peroxide was poured through the filter, which was then washed two or three times with hot water. The filter was then transferred to a beaker, broken up with a glass rod, and heated with 50 c.c. of a saturated solution of bromine in dilute hydrochloric acid (1:1); the liquid was then filtered through a small filter into the alkaline liquid in the original flask, and the filter was pressed down with a glass rod, and washed with hot water. The united filtrates were decolorised with sulphurous acid, 20 c.c. of citric acid solution (100 grms. dissolved in 200 c.c. of water) were added, followed by an excess of ammonia, 10 c.c. of potassium cyanide solution (saturated), 5 c.c. of ammonium sulphide, 25 c.c. of ammonium chloride solution (20 per cent.), and, finally, 8 grms. of hydrosulphite; the liquid was then boiled for one minute, 1 or 2 grms. more hydrosulphite added, and the precipitated stannous sulphide was allowed to settle, filtered off and determined as usual, 10 c.c. of citric acid and 30 c.c. of potassium iodide solution being used in the diluting solution in the last stage.

The following results were obtained:

Steel taken Grms.	Tin added Grm.	Antimony added Grm.	Titration c.c.	Tin found Grm.	Tin added Per Cent.	Tin found Per Cent.
5·0	Blank	0·05	0·5 ($N/100$)			
Blank	Blank	0·05	0·3 ($N/100$)			
5·0	0·0040	0·05	6·8−0·3−0·2=6·3 ($N/100$)	0·0038	0·080	0·076
5·0	0·0030	0·05	5·4−0·3−0·2=4·9 ($N/100$)	0·0029	0·060	0·058
5·0	0·0020	0·05	4·1−0·3−0·2=3·6 ($N/100$)	0·0021	0·040	0·042
5·0	0·0010	0·05	2·2−0·3−0·2=1·7 ($N/100$)	0·0010	0·020	0·020
20·0	0·0010	0·05	2·7−0·3−0·8=1·6 ($N/100$)	0·0009	0·0050	0·0045

The significance of the two "blanks" and of the two sets of figures deducted from the titration results is as follows:—The test made on the steel used, without addition of tin, and with the conditions otherwise the same, required 0·5 c.c. of $N/100$ iodine solution; the test made on the antimony alone without addition of either steel or tin required 0·3 c.c.; the difference between these two figures, 0·2 c.c. $N/100$ iodine, represents tin present in the sample of steel used as a basis, and therefore, whilst being peculiar to this particular series, had to be deducted from the titration values of those tests which were carried out on 5 grms. of steel; in the case where 20 grms. of steel were used, the 0·2 c.c. had, of course, to be multiplied by 4. The 0·3 c.c., representing tin contained in the antimony solution, is a general reagent blank, and had to be deducted from all the determinations indiscriminately, and, of course, from any that might be carried out with the same antimony solution. With an unknown antimony solution it is necessary to determine the blank.

Recovery of Tin from Organic Acid Solution.—As has been already stated, hydrosulphite methods have not, up to the present, proved amenable for the complete separation of antimony and tin. One of the best of the older processes for this purpose is Clarke's method of precipitating the antimony with hydrogen sulphide, in presence of a large excess of oxalic acid; this process, whilst excellent so far as antimony is concerned, has the serious drawback that the oxalic acid has to be destroyed before the tin can be recovered. The hydrosulphite process, taking place, as it does, entirely in alkaline solution, is especially adapted for the recovery of tin from this solution. Some trials were made with 0·2 grm. of antimony and varying amounts of tin; after Clarke's separation had been carried out, the filtrate was made alkaline with ammonia, 5 c.c. of saturated potassium cyanide solution were added, and 5 c.c. of ammonium sulphide, followed by about 8 grms. of hydrosulphite. The solution was boiled for 1 minute, 2 or 3 grms. more hydrosulphite were added, and the precipitate was allowed to settle on the steam-bath and then filtered off and the determination was finished as usual. The results were as follows:

Antimony taken Grm.	Tin added Grm.	Titration c.c.	Tin found Grm.	Tin added, Per Cent.	Tin found Per Cent.
0·20	0·010	15·8 (*N*/100)	0·0094	5·0	4·7
0·20	0·008	12·8 (*N*/100)	0·0076	4·0	3·8
0·20	0·006	9·8 (*N*/100)	0·0058	3·0	2·9
0·20	0·004	6·5 (*N*/100)	0·0039	2·00	1·95
0·20	0·002	3·3 (*N*/100)	0·0019	1·00	0·95

A point which emerged during this work was the absolute necessity of working with *hot* concentrated solutions of oxalic acid in carrying out Clarke's separation; on trying it with cold saturated oxalic acid solution less than half of the tin was sometimes recovered. Most text-books, whilst giving correct directions, do not seem to stress this point as it deserves.

The Relative Vitamin *A* and Vitamin *D* Content of Samples of Cod-Liver Oil*

By KATHARINE H. COWARD, D.Sc., F. J. DYER, B.Sc., and
BARBARA G. E. MORGAN

For many years the "blue value" of a sample of cod-liver oil (obtained by the action of antimony trichloride upon it) has been accepted as, at least, an approximate measure of the vitamin *A* content of the oil. This would appear to be justified only in so far as an oil with a high blue value has usually been found to have a high vitamin *A* value (as measured biologically), and an oil with no blue value has been found to have no vitamin *A* value. Latterly, however, since the biological method of estimating vitamin *A* has been rendered more accurate, serious doubt has been thrown on the degree of correlation between the blue value of an oil and its true vitamin *A* value.

Moreover, much work has been carried out that shows that (*a*) the blue value of an oil may be decreased by the presence of certain other substances in the oil (Drummond and Hilditch,[1] 1930; Norris and Church,[2] 1930), and (*b*) the blue colour obtained in this test is due to the absorption bands of two substances, one of which is known to be influenced by certain processes (such as the blowing of ozonised oxygen through the oil), whilst the other is not influenced by these particular processes (Heilbron, Gillam and Morton,[3] 1931). The band which is not thus influenced appears to be associated with the absorption band $328m\mu$ of the oil—the band whose intensity, so far, has shown the best agreement with the vitamin *A* value of an oil. Even if the vitamin *A* in a particular oil gives rise to a certain "blue value," the "blue value" of the oil itself may be greater or less than that due directly to the vitamin as such. It is not surprising, therefore, that the more accurate measurements of vitamin *A* in oils should fail to agree well with the "blue values" of those oils. The practice of converting a "blue value" into a vitamin *A* value simply by multiplying it by a constant factor is, at least, unsafe. To call the result "biological units" implies the performance of a biological test, which is wholly misleading.

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* Communication from the Pharmacological Laboratories, Pharmaceutical Society of Great Britain.

The procedure of multiplying the "blue value" by another constant and calling the result vitamin *D* units is still more unsound. It rests simply on the assumption that if an oil is rich in vitamin *A*, it will be proportionately rich in vitamin *D*. The only evidence of this to be found in the literature is a statement of Drummond and Hilditch[1] (1930) in their report to the Empire Marketing Board on the "Relative Values of Cod Liver Oils from Various Sources." In it, they state that "generally speaking, there is a parallelism between the vitamin *A* and vitamin *D* potencies of the oils, although a few exceptions are to be noted. Thus, the Norwegian oils, L and Q, are of low vitamin *A* value, but relatively good as sources of *D*." Now a general trend in a correlation between two factors is unsafe as a basis for exact comparisons. The figures of Drummond and Hilditch have only to be examined to show how true this statement is. Oils of the same vitamin *A* value have a vitamin *D* value ranging from 100 to 300 units per grm., which is almost the full range of possible vitamin *D* values of samples of cod-liver oil. Similarly, oils with 200 vitamin *D* units per grm. have vitamin *A* values ranging from 100 to 1000 U.S.P. units. Yet, despite the evidence of these figures and the warning clearly stated by the writers in their report, it has been assumed by some that the vitamin *A* and *D* values run parallel to each other, and that both may be measured by the "blue value" of the oil.

EXPERIENCE OF THE PHARMACOLOGICAL LABORATORIES

To prevent this misconception from gaining further acceptance, it seemed advisable to review the results of the estimation of vitamins *A* and *D* in cod-liver oils carried out in these laboratories.

(*a*) VITAMIN *D*.—Since February, 1927, estimations of vitamin *D* have been made in terms of a standard of reference (a solution of irradiated ergosterol prepared by the National Institute for Medical Research), which was accepted in August, 1930, by the Medical Research Council of Great Britain (*B.M.J.*, *Lancet*, *Pharm. J.*, Aug. 30, 1930; ANALYST, 1930, **55**, 692), and in October, 1931, by the Permanent Commission on Biological Standardisation of the Health Organisation of the League of Nations (*cf.* ANALYST, 1932, 173). Thus, all the samples of cod-liver oil examined in these laboratories for vitamin *D* have been assayed in terms of the international standard, and the results expressed in international units, the unit being defined as the antirachitic activity contained in 1 mgrm. of the international standard. Many samples of cod-liver oil have been submitted for vitamin *D* tests only, and the "blue values" of some of these were not determined at the time of the biological examination. They could not, therefore, be included in this review. Those that are included had their "blue colour values" determined at the same time as, or within a month of the biological examination. The results are collected in Table I.

TABLE I

Oils with blue value of:—	Vitamin *D* potency of these oils—units per grm.	Average
4 to 5	88, 100, 100, 150	109·5
6 to 7·5	56, 64, 82, 100, 100	80·4
8 to 10	56, 60	58·0
11 to 15	88, 100, 100, 150	109·5
17 to 20	40, 50, 120, 200, 250	132·0
20·5 to 25	100, 110, 180, 180, 210	156·0
28	200	200
34·5	110	110
45	50	50
50	7·5*	7·5*
107·5	100	100

* Did not smell like cod-liver oil, but had actually been sold as such.

It is evident from Table I that some oils may have the same blue value as other oils, but twice, or even six times, the vitamin *D* value. Even if averages of these values are taken, there is no evidence that a higher vitamin *D* value is associated with a higher blue value. In fact, it will be seen that there is not even a trend of the vitamin *D* values to follow the blue values.

(*b*) VITAMIN *A*.—We have made a similar comparison of the results obtained to date of the vitamin *A* content of oils. Many of these results have already been reported in a paper by Coward, Dyer, Morton, and Gaddum[4] (1931). In this paper it was shown that serious discrepancies may exist between the biological values for vitamin *A* and the "blue values" of the oils. Since then, further examinations of oils have been made by the same method, details of which are to be presented in a second paper. In particular, four oils have been examined with increased refinement of technique, which, we think, can leave no doubt as to the unsoundness of relying on the "blue value" of an oil as a measure of its vitamin *A* potency. The results are collected in Table II. The vitamin *A* potency of each oil has been provisionally expressed in units, the unit being the vitamin *A* activity of 1γ (0·001 mgrm.) of the sample of carotene issued by the National Institute for Medical Research in December, 1930, to certain laboratories for investigation of the possibility of adopting carotene as a standard of reference for vitamin *A*. It is unlikely that the standard preparation of carotene, when issued, will differ materially from the one used in these investigations.

TABLE II

Oil	Colour value of oil (*a*)	Vitamin *A* potency of these oils (*b*)	Colour value relative to oil 1 (= 100) (*c*)	Vitamin *A* potency relative to oil 1 (= 100) (*d*)
1	4·1	1564	100	100
2	4·4	1568	107	100
3	7·6	3098	185	198
4	9·0	3140	220	201
5	10·2	4916	249	314
6	10·8	2596	263	166
7	11·6	2000	283	121
8	15·2	3510	371	225
9	17·4	2440	424	156
10	20·6	5800	500	352
11	28	3054	683	195
12	86	12546	2098	802
13	305	31246	7439	1998

The figures in Table II demonstrate the *trend* of the vitamin *A* value to follow the colour value, but a comparison of the figures of columns (*c*) and (*d*) shows the serious discrepancy that may occur between the two values for any one oil. A statistical examination of the accuracy of our biological test for vitamin *A* shows that, by the use of ten animals for a test of one dose of a substance, the result will be 21 times out of 22 between 60 and 160 per cent. of the true value. For each test reported in Table II, never less than nine, and often more than ten rats, were used. It is probable, therefore, that the colour values of oils 1, 2, 3, 4, and 5, and possibly 8 and 10, may be said to agree with the biological values. It is evident, however, that in the rest (6 out of 13 samples) the blue values lie well outside the range of the possible biological values. The discrepancies between the blue values and the biological values of these oils must be regarded as serious.

Four other oils have been examined within the last six months, each time in comparison with the standard oil. That is, a fresh test of the standard was made at the same time as the test of each of the four samples. Moreover, each comparison was made by using equal numbers of rats from the same litters for the test sample and for the standard. The values obtained for these four samples are collected in Table III.

TABLE III

Oil	Colour value of oil	Vitamin *A* potency of oil	Colour value relative to oil 1 (= 100)	Vitamin *A* potency relative to oil 1 (= 100)
1	17·1	11400	100	100
2	19·6	8800	114	77
3	21·4	3000	125	26
4	23·0	6280	135	55

It is of interest to note that the "colour value" of the oil which we have used as a standard of reference in all this work has changed only very slightly during three years. The oil has been kept in the dark at room temperature for two years, and in cold store for the last twelve months.

The results in Table III show even wider discrepancies between blue values and biological values than do those in Table II. One oil with a blue value of 125 per cent. of that of another oil, has a biological value only 26 per cent. of that of the second oil. The oils do not even demonstrate a trend of a high biological value to be associated with a high blue value.

SUMMARY.—The examination of 30 samples of cod-liver oil shows that the "blue colour value" of the oil is no indication of its vitamin *D* potency.

The examination of 17 samples of cod-liver oil shows, on the whole, a definite trend of a high blue value to be associated with a high vitamin *A* value, but it is possible for oils of the same colour value to have vitamin values differing by as much as·400 per cent. Thus, the blue colour value of an oil cannot be considered a measure of its vitamin *A* potency. Moreover, the vitamin *D* values of different samples of cod-liver oil are not proportional to the vitamin *A* values.

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The Nitro-Chromic Acid Reaction for the Detection of Primary and Secondary Alcohols, with Special Reference to Saccharides

BY WILLIAM ROBERT FEARON, SC.D., F.I.C., AND
DAVID MICHAEL MITCHELL, B.A.

WHILE it has been known for many years that solutions of chromic acid are readily reduced by compounds of the alcohol type, the scope and conditions of the reaction are not yet fully investigated. When a sugar solution of about 1 per cent. concentration is treated with an equal volume of concentrated nitric acid and a few drops of a 5 per cent. solution of potassium dichromate, a blue colour develops in less than a minute in the cold solution. This reaction, which we observed for the first time recently, is given by all saccharides and other compounds containing a primary or a secondary alcohol group. On reviewing the literature, it was found to be similar to a reaction described by Agulhon (*Bull. Soc. Chim.*, 1911, **9**, 881), but it is capable of a much greater degree of specificity than he appears to have realised.

SCOPE OF THE REACTION.—According to Agulhon, the reaction is given by all aldehydes, by all primary, secondary, and tertiary alcohols, and by all aliphatic compounds containing aldehyde or alcohol groups. Aliphatic ketones react also, but require a longer time. During our independent investigation of the reaction it appeared probable that the test can be applied so as to distinguish primary and secondary alcohols from tertiary alcohols, a conclusion in accordance with what is known regarding the relative stability towards oxidation exhibited by each of these three classes of compounds. We may use a reagent consisting of 5 per cent. potassium dichromate in nitric acid, diluted 1: 2, and add 5 c.c. of the reagent to 1 c.c. of the solution to be tested; or we may employ a 5 per cent. solution of potassium chromate instead of the original dichromate. This modification we have studied under the name of the nitro-chromic acid test.

THE NITRO-CHROMIC ACID TEST.—Five drops of 5 per cent. potassium chromate solution are added to 5 c.c. of nitric acid previously diluted in the proportion of 1 to 2 with water, and cooled. Then 0·1 to 1·0 c.c. of the solution to be tested is added, and the mixture is shaken. A positive result is shown by the development of a blue or blue-violet colour within 1 to 5 minutes, depending on the dilution. The test is positive with all of the familiar primary and secondary alcohols, with all saccharides, with formaldehyde, and with hydroxy acids, such as lactic and tartaric acid. The test is negative with tertiary alcohols, aldehydes other than formaldehyde, aliphatic ketones, oxalic acid, citric acid, and the acids of the acetic series, amino acids and amino compounds, such as urea, polymeric compounds, such as paraformaldehyde, metaldehyde, and (under restricted conditions) the polysaccharides. Phenols do not give the blue colour, although they interact variously with the nitric acid.

Nitrites, peroxides, and hypo-halites also develop a blue colour with the reagent—a reaction which is quite distinct from the ultramarine-blue colour of the familiar peroxide test for chromium salts.

Oxalates react anomalously. No blue colour appears within the first few minutes, but when the mixture has been kept for several hours a dichroic purple colour develops. Apart from these exceptions, the test appears to be specific for the groups $-CH_2.OH$ and $=CH.OH$, the response of formaldehyde being attributable to enolisation.

APPLICATION OF THE TEST.—1. *Distinction between Primary, Secondary and Tertiary Alcohols.*—The test is sufficiently specific not to be given when a drop of a pure tertiary alcohol is added to 5 c.c. of the cold reagent, although primary and secondary alcohols react readily in 0·1 to 1·0 per cent. concentration. The test may also be applied to show the presence of impurities in specimens of tertiary alcohols.

2. *Distinction between Hydroxy and Non-hydroxy Acids and Differentiation of Hydroxy Acids.*—The test will distinguish rapidly between tartaric and citric acids, the former reacting positively.

3. *Distinction between Carbohydrates and other Bio-organic Compounds such as Fats and Proteins.* Carbohydrates, unlike fats and proteins, give a positive reaction. Normal urine does not give the reaction; nor does blood serum, as the sugar content is below the critical limit of the test.

4. *Distinction between Saccharides and Polysaccharides.*—Insoluble polysaccharides, such as cellulose, do not give the reaction; soluble polysaccharides, such as starch, inulin and dextrins, give the reaction in accordance with their instability towards the acid in the reagent. Thus, by reducing the concentration of nitric acid, it is possible to obtain a mixture which reacts rapidly with saccharides and not with polysaccharides, but this is partly determined by the concentration of carbohydrate. With nitric acid diluted with water (1:4), a 1 per cent. solution of glucose or maltose gives the blue coloration within 5 minutes, whereas a 1 per cent. solution of starch may remain for several hours without reducing the chromic reagent. The observation is of interest on account of the hypothesis advanced by Haworth (*The Constitution of the Sugars*, 1929), that the polysaccharide is composed of conjugated saccharide units, joined by co-valent links. The relative slowness of reaction with the chromic reagent indicates that the $-$CH.OH groups in the polysaccharide complex are masked in some manner.

Delicacy of the Test.—The time taken for the development of the blue colour increases greatly with the dilution of the alcohol. Taking 1 minute as the time-limit, a positive result is obtained with primary alcohols in 0·1 per cent. concentration; with secondary alcohols in 0·5 per cent. concentration; and with saccharides in 1·0 per cent. concentration. Extending the time-limit to 1 hour, a positive result may be obtained with ethyl alcohol in 0·01 per cent. concentration; and with glucose in 0·08 per cent. concentration.

Mechanism of the Test.—A discussion of the mechanism is outside the scope of the present paper. That the colour of blue pigment produced differs from the ultramarine-blue coloration formed in the peroxide test for chromates is shown by its insolubility in ether, and by the fact that the peroxide pigment is bleached by strong acids. The pigment itself is, presumably, the anhydride of nitrous acid formed under conditions comparable with those of the Debus reaction for the preparation of glyoxylic acid by the oxidation of alcohol with excess of nitric acid. The chromium salt determines the specificity of the test. When a dichromate is used, and introduced after the other reactants have been mixed, or is added in excess, as in the original Agulhon reaction, the test loses its specificity, owing, presumably, to the action of the chromic anhydride.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

NITRATES IN MILK AS EVIDENCE OF ADDED WATER

As recorded in the Annual Report of the County Analyst for Somerset for 1931 (ANALYST, 1932, 247), one sample of milk contained nitrates but showed no evidence of added water. My attention has been called by Mr. H. H. Bagnall, B.Sc., F.I.C., City Analyst of Birmingham, to the practice, on the part of milk producers, of adding saltpetre to milk to remove the taste and smell given by feeding on turnips, and enquiry showed that the producer of this milk was in the habit of adding a small amount of saltpetre in the summer months to keep the milk sweet. The sample was collected in August.

The above instance shows the importance of making inquiries, and also shows that accidental contamination with nitrates did not occur with this sample; it did not occur with any of the other 469 samples, so that it is an extremely unlikely contingency (*cf.* G. D. Elsdon and J. A. Sutcliffe, ANALYST, 1913, **38**, 451; G. D. Elsdon and P. Smith, ANALYST, 1922, **47**, 18; and G. D. Elsdon, ANALYST, 1923, **48**, 115).

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D. R. WOOD.

FLUORESCENCE OF MILK AND BUTTER IN ULTRA-VIOLET LIGHT

1. Our experience in these laboratories with Kelvin, Bottomley and Baird's quartz lamps during the past twelve months has shown that the fresh milk of the cow, goat or sheep exhibits a canary-yellow fluorescence, but we are unable to agree with Popp (ANALYST, 1926, **51**, 540) that this is an attribute of the fat.

2. Skim-milk whey retains much of the original fluorescence, but the separated cream is of a much paler yellow than the whole milk. This point is strikingly demonstrated in the Gerber butyrometer, where the column of fat is devoid of the yellow fluorescence, whilst the acid liquid, which is dark brown in daylight, is bright canary-yellow in ultra-violet light.

3. If fresh milk, either skimmed or whole, is kept in a test tube at the ordinary temperature for a day or more, the yellow fluorescence gradually gives place to a bluish colour, developing from the bottom upwards. If, however, the milk is boiled, or if formalin is added, this change does not take place.

4. If this "blue" milk is now shaken in the tube the yellow fluorescence at once returns, but gives place to blue again on standing for an hour or so. If, however, air is removed by means of a pump from the tube containing the regenerated yellow milk, the change to blue is very rapid.

5. A sample of curd cheese, which also exhibited a superficial bright yellow fluorescence, showed blue fluorescence, quickly changing back to yellow on exposure of a freshly-cut surface. This cheese, when repeatedly washed, lost most of its yellow fluorescence, which was transferred to the washing water.

6. Control experiments in an atmosphere of carbon dioxide or of nitrogen have shown that oxygen is the active agent in the regeneration of the yellow

fluorescence. Its destruction would appear to be due to an agent similar to that which decolorises methylene blue in the "reductase test," and in this connection it has been found that the methylene blue will also regain its colour on aeration.

7. The colour of milk-fat, including ordinary churned butter and native samneh (rendered butter-fat), in ultra-violet light has shown variations between creamy white and yellow, which are often, but not always, accentuations of the shades of colour observed in daylight.

8. Samples of coconut fat have shown an intense blue fluorescence, and in experimental tests as little as 5 per cent. of this fat was found to affect the colour of butter-fat, although from 10 to 20 per cent. was required to give a definite indication of adulteration when the exact tint of the original pure butter was unknown.

9. As a result of the examination of 959 samples, most of which were native samneh, we find that a bluish tint is a fairly reliable indication of adulteration, whilst the absence of any suggestion of yellow is to be viewed with suspicion. Actually, of 89 adulterated samples, 86 exhibited some degree of bluish fluorescence, whilst of the 870 genuine samples 99 per cent. had a fluorescence ranging from creamy white to yellow.

10. Samples of freshly-rendered butchers' fat from the cow, sheep and goat could not be placed definitely outside the colour range of butter, but, after being kept for a month, they all developed a dirty blue fluorescence, although, apparently, they were still in good condition.

11. Artificial colouring matter may mask the fluorescence, but the coloured fats so far met with have yielded to treatment with boiling water and charcoal (0·3 grm. of charcoal to 10 grms. of fat). The charcoal may impart a blue fluorescence to the water, but this does not interfere with the colour of the fat.

12. In carrying out the fluorescence test we use, for comparison, standard samples of adulterated and pure butter-fat. In doubtful cases differences are often accentuated if the fats for comparison are spotted in a semi-solid state, side by side, on a sheet of paper.

13. There are many avenues for further investigation, and there may be disturbing factors not yet encountered, but we have so far found the test to be of considerable practical value; more so, perhaps, than any other single routine test, with the exception of the determination of the volatile fatty acids. Under conditions obtaining here, for example, the taking of large numbers of unofficial samples is often useful as a means of indicating the vendors who require further attention, and, in such cases, a rapid test of this kind is invaluable, so long as its limitations are recognised.

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THE SOLUBILITY OF URANYL ZINC SODIUM ACETATE IN ALCOHOL OF DIFFERENT STRENGTHS

For the determination of sodium as uranyl zinc sodium acetate, and also in the colorimetric determination of sodium, a knowledge of the solubility of the triple salt in alcohol of different strengths is important.

The interference of alcohol in the microchemical method of comparing the colour developed from an amount of triple salt equivalent to 0·1 mgrm. of sodium, in water, with that produced from the same amount of salt in alcohol of different strengths, is shown in the following table. The standard was set at 30 mm. in the colorimeter, and the average of four readings was taken.

Alcohol. per cent. by vol.	Average reading. mm.	Average error. Per Cent.
0	30	0
10	28·6	4·7
20	27·0	10·0
30	25·8	14·0
40	23·4	22·0
50	20·8	30·7

The solubility of the triple salt was determined by evaporating to dryness 10 c.c. of the saturated solution. The results at 25° C. are given in the following table:

Concentration.	Solubility in 100 c.c. Grm.
Absolute alcohol	0·132
96 per cent. by vol.	0·042
90 " " " "	0·062
80 " " " "	0·119
70 " " " "	0·194
60 " " " "	0·316
50 " " " "	0·967

UNIVERSITY OF STELLENBOSCH,
S. AFRICA.

G. W. B. VAN DER LINGEN.

THE COMPOSITION OF LINSEED OIL

IN a paper by N. E. Cocchinaras on "The Composition of Linseed Oil" in the April number of THE ANALYST, p. 234, appeared the statement, attributed to me, that linseed oil contains 4 per cent. of oleic acid, 20 per cent. of palmitic acid, and 51·7 per cent. of stearic acid; moreover, the reference should be *J. Soc. Chem. Ind.*, 1913, **32**, 1091, and not ANALYST, 1914, **39**, 70.

If the author had read my paper he would have found that the percentages of stearic and palmitic acids were 4·1 and 1·3, respectively. The saturated acids obtained from the lead salts of Calcutta oil were found to be 6 per cent., with melting-point of 53–55° C. In the examination of oil from British-grown linseed (Eyre and Morrell, *Publications of the British Flax and Hemp Growers' Society*, No. VI, 1918) the percentage of saturated glycerides in English-grown linseed was given as 4 per cent. Unpublished results show that the oil obtained from seeds of different stages of ripeness from English-grown linseed (special variety of La Plata seed produced at Wye) had the following characteristics:

BRITISH-GROWN LINSEED FROM WYE (KENT) SUPPLIED BY DR. EYRE

	Unripe seed	Seed ripened on the stalk	Seed fully ripened before picking	Calcutta oil
Percentage yield of oil ..	27·8	33·3	34·0	—
Sp.gr. at 15°/15° C. ..	0·9337	0·9320	0·9317	0·9329
Acidity, per cent.	1·98	—	0·568	1·54
$n_D^{14°\text{-}15°}$	1·4819	1·4847	1·4849	1·4830
Saponification value ..	190·5	—	189–191	192–193·5
Iodine value (Wijs), 1½ hours	185–186	190–194·5	188	189–190
" " 24 "	189	193	196	191·4
Percentage of saturated acids	3·4	3·6	4·5	7·56

The yield of the oil increases with ripening, with slight increase in the iodine value, and also in the percentage of saturated acids. A sample of Calcutta oil contained 7·56 per cent. of saturated acids. As the iodine values of oils from different countries vary, so do the percentages of saturated acids.

R. S. MORRELL.

TOR LODGE, TETTENHALL WOOD,
WOLVERHAMPTON.

Official Appointment

THE Minister of Health has approved the following appointment:

ALAN WEST STEWART, D.Sc., A.I.C., as Public Analyst for the Boroughs of Newbury and Windsor (New), in place of Sir W. R. Smith (deceased), (May 24th, 1932).

Ninth Report of the Essential Oil Sub-Committee to the Standing Committee on Uniformity of Analytical Methods

THE DETERMINATION OF CARVONE AND MENTHONE

THE investigations of the Essential Oil Sub-Committee on the determination of ketones in essential oils have shown that, in the case of carvone and menthone, the hydroxylamine method gives results which approximate very closely to the actual content. The oxime formation takes place slowly in the cold, but is accelerated by heat. It proceeds most rapidly when the liberated acid is neutralised at frequent intervals. It has been found necessary, in order to obtain accurate results, to standardise the conditions very carefully. Particularly is it essential to allow the reaction to proceed for a definite time only, as experiments appear to indicate that a secondary reaction takes place very slowly and continues for some hours.

The Sub-Committee recommends the following method for the determination of carvone in caraway oil, dill oil and spearmint oil, and for menthone in peppermint oil.

The following solutions are required:

Indicator Solution.—A 0·2 per cent. solution of dimethyl yellow (*p*-dimethylaminoazobenzene) in 90 per cent. alcohol.

N Alcoholic Potash.—Prepared with 90 per cent. (by volume) alcohol and standardised against *N* hydrochloric acid, using dimethyl yellow as indicator and running the alkali *into* the acid until the full yellow colour is obtained.

N Hydroxylamine Hydrochloride Reagent.—Dissolve 6·95 grms. of pure hydroxylamine hydrochloride in 95 c.c. of 90 per cent. (by volume) alcohol, add 0·4 c.c. of dimethyl yellow solution, and adjust to the full yellow colour of the indicator with *N* alcoholic potash, and make up to 100 c.c. with 90 per cent. (by volume) alcohol.

The full yellow colour of the indicator may be defined as that colour which is not changed by the further addition of alkali.

The alcohol used must be free from aldehydes and ketones.

METHOD OF DETERMINATION.—Weigh out exactly into a stoppered tube (approximately 150 mm. long by 25 mm. in diameter) about 1·5 grms. of caraway, dill or spearmint oil, or 3 grms. of peppermint oil; add 20 c.c. of the *N* hydroxylamine hydrochloride reagent, and titrate with *N* alcoholic potash until the red colour changes to yellow. Place the tube in a water-bath at 75° to 80° C.,* and neutralise the liberated acid with *N* alcoholic potash at five-minute intervals; at the expiration of 40 minutes complete the titration to the full yellow colour of the indicator and note the reading of the burette.

Two determinations should be carried out side by side, using two burettes, and the one first completed, *plus* a slight excess of alcoholic potash (0·5 c.c.), should be used as a colour standard for the end-point of the duplicate. The percentage should be calculated from the duplicate determination.

The number of c.c. of *N* alcoholic potash required, multiplied by the correcting factor 1·008, by the factor 0·150 for carvone or 0·154 for menthone, and by 100, and divided by the weight of oil taken will give the percentage (by weight) of the ketones calculated as carvone or as menthone.

The correcting factor is necessary, owing to the fact that the end-point of the titration occurs at a *p*H different from that of normal hydroxylamine hydrochloride.

Determinations made by members of the Sub-Committee lead us to the opinion that the maximum variation with this method should not exceed ±1 per cent. The following tables show the results obtained by members of the Sub-Committee on samples circulated for collective testing:

PERCENTAGE OF MENTHONE IN PEPPERMINT OIL

Sub-Committee Member	Raw American oil	Japanese oil	Saponified and distilled American oil
No. 1.	23·7	33·4	22·1
	23·3		21·8
No. 2.	21·6	32·5	21·1
No. 3.			21·8
			21·1
No. 4.	22·5	32·3	
	22·4	32·1	
	22·3	32·7	
	22·3	32·2	
No. 5.	22·3	31·9	22·1
	22·3		22·2
	21·9		
	21·9		
No. 6.		31·6	23·4
			23·3
No. 7.			21·8
			21·7
No. 8.	22·0	31·8	22·1
	21·9	32·6	
	22·2	31·8	
Variation	21·6 to 23·7	31·6 to 33·4	21·1 to 23·4
Mean	22·3	32·3	22·0

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* A beaker of water standing on a boiling water-bath provides a suitable water-bath at a temperature of 75° to 80° C.

PERCENTAGE OF *d*-CARVONE

Sub-Committee Member	Purified *d*-carvone	*d*-Carvone mixture containing 55·45 per cent. of *d*-carvone	Caraway oil	
No. 1.	98·9	54·7	57·9	
	99·0	55·1		
No. 2.	99·3	55·6	57·0	
			57·2	
No. 3.			57·1	
		55·8	57·1	
			57·5	
No. 4.	99·2	54·9	57·2	58·1
	99·7	55·6	57·3	58·2
	99·8	55·1	57·4	58·7
	99·7	56·2	57·4	
No. 5.	99·8	55·3	57·6	58·4
	99·9	55·7	57·6	58·5
	100·3	55·7	58·0	58·7
	99·9	55·7	58·2	58·9
	99·9		58·4	
No. 6.	99·9	56·0	58·2	
	100·4	56·4	58·6	
No. 7.	99·5	54·7	59·0	
	99·7	54·5		
No. 8.	99·8	55·5	58·0	
	99·9	55·8		
No. 9.	98·3			
	99·3	54·5		
	98·7			
	100·3			
No. 10.	98·7			
	99·4			
Variation	98·3 to 100·4	54·5 to 56·4	57·0 to 59·0	
Mean	99·55	55·4	57·9	

PERCENTAGE OF *l*-CARVONE

Sub-Committee Member	*l*-Carvone mixture containing 52·1 per cent. of purified *l*-carvone	Spearmint oil
No. 1.	53·4	64·0
		64·5
No. 2.	53·1	
No. 3.		62·5
		62·6
No. 4.	53·3	64·9
	53·1	
	53·5	
	53·5	
No. 5.	52·2	
	51·6	
No. 6.	51·7	65·0

PERCENTAGE OF *l*-CARVONE—*continued*

Sub-Committee Member	*l*-Carvone mixture containing 52·1 per cent. of purified *l*-carvone	Spearmint oil
No. 7.	52·1	64·2
	52·5	65·0
	52·2	64·6
	52·8	
Variation	51·6 to 53·5	62·5 to 65·0
Mean	52·7	64·1

(*Signed*),

John Allan (Chairman), C. T. Bennett, S. W. Bradley, E. Theodore Brewis, L. E. Campbell, Thos. H. Durrans, T. W. Harrison, Ernest J. Parry, C. Edward Sage, W. H. Simmons, T. Tusting Cocking (Hon. Sec.).

May 1932.

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

POISONING BY CASTOR SEED

LIABILITY OF PERSON DELIVERING A DANGEROUS ARTICLE

J. TAYLOR & SONS, LTD., *v.* UNION-CASTLE MAIL STEAMSHIP CO., LTD.

IN this action, which was decided on February 17th, 1932, a firm of forage merchants sued the defendants for alleged negligence, claiming £430 damages. In September, 1930, a steamship belonging to the defendants arrived in London with a cargo of maize and other grain, coffee and castor seeds, from Mombasa. The castor seed was shipped with a notice in red ink to the effect that it must be kept separate from the other cargo. On arrival, the Port Authority swept up the grain left on the floor of the hold and divided it *pro rata* among the different holders of bills of lading.

The defendants gave a delivery order to a firm holding a bill of lading for 3584 bags of maize, and this firm sold to the plaintiffs 15 bags, which were, in fact, part of the bags of loose collected cargo, and the plaintiffs mixed these with other grain in the ordinary course of business. A parcel was then sold to a customer, who fed his horses on the grain, with the result that 6 died and 22 were made ill, owing to castor poisoning. It was proved that the grain contained 0·22 per cent. of castor seed, and the plaintiffs settled the claim of their customer for £430, which they now endeavoured to recover from the defendants.

Mr. Justice MacKinnon, in giving judgment for the defendants, said that the extent of the obligation of a person who delivered a dangerous article, to give warning of its nature, must vary with his occupation; for example, it would be higher in the case of a chemist selling a dangerous article than in the case of a layman. The question must be whether the person delivering the article knew, or, as a reasonable man, ought to have known, that it was dangerous. Here the defendants were not dealers in grain and experts in that particular trade, but were shipowners carrying goods of every possible description.

With regard to the degree of general knowledge of the danger of castor beans, he might say that until the hearing of this case he, himself, knew nothing of that danger; and the evidence had satisfied him that the knowledge was not widely spread. He thought, therefore, that it would be wrong to hold shipowners liable for not warning forage dealers, who might reasonably be supposed to have expert knowledge themselves.

POTTED MEAT PASTE SOLD AS POTTED BEEF

On May 2nd, a manufacturer of potted meat pastes was summoned at Sheffield Police Court for having sold, by the hands of an agent, to a tradesman an article described as "potted beef," but containing 3·9 per cent. of anhydrous starch. There were also summonses against the agent and the tradesman for selling potted beef which contained 4·6 per cent. of anhydrous starch and 71·5 per cent. of water.

The inspector who bought the samples stated that three years ago circulars were sent to the manufacturers of potted beef in Sheffield, advising them that starch should not be an ingredient of potted meat, and also that there should not be more than 70 per cent. of water in potted beef.

Mr. John Evans, F.I.C., Public Analyst for Sheffield, said that starch was a foreign substance in potted meat. There was no legal standard for the amount of water in potted beef, but anything over 70 per cent. was exceptional. He would have taken no exception to the sample being sold as "potted meat paste."

The works-manager of a firm manufacturing various grades of potted beef said that in the best quality they tried to keep the amount of water as near 50 per cent. as possible, and in the cheapest quality it was 65 per cent. They did not introduce starch.

The solicitor for the defence pleaded "guilty" in the case of the tradesman, since the product had been labelled "potted meat" after it had been supplied to him. But the difference between "potted beef" and "potted beef paste" had not been explained to him.

The manufacturer stated that, in the preparation of the paste, 2 lbs. of biscuits were used with 60 lbs. of meat, and that all his wares were described as "potted meat paste."

The magistrates said that they gave the benefit of an element of doubt to the manufacturer and his agent, and would dismiss the cases. The tradesman was fined £5.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Buckwheat Milling and its By-Products. M. R. Coe. (*U.S. Dept. of Agric., Circular No.* 190.)—Buckwheat, *Fagopyrum esculentum*, is milled for flour and groats, and the shorts or middlings, which make up the portion of the grain immediately inside the hull, after separation from the flour, are used as feeding stuffs for cattle. The middlings are a valuable food, containing the oily covering of the grain and germ, but vitamins *A* and *D* are absent, or present only in small quantities. Too large a proportion of hull must not be present in feeding stuffs, and these hulls are usually burned, although sometimes used as packing material.

The following are typical compositions of buckwheat grain and its products:

Buckwheat grain—	Water Per Cent.	Ash Per Cent.	Fat Per Cent.	Protein Per Cent.	Fibre Per Cent.	Nitrogen-free extract Per Cent.
Japanese whole grain ..	10·05	1·71	2·36	10·69	11·37	63·82
Silverhull whole grain ..	10·01	1·81	2·43	11·81	9·92	64·02
Tartary whole grain ..	11·06	1·64	2·32	10·19	15·21	59·58
Buckwheat flour—						
Very light	12·65	0·61	0·05	4·73	0·39	81·12
Light	13·15	1·17	1·29	7·19	0·59	76·61
Medium	12·06	1·37	1·85	9·75	0·96	74·01
Dark	11·67	1·21	1·82	8·94	1·04	75·32
Very dark	13·94	2·21	3·33	15·94	1·21	63·37
Buckwheat hulls—						
Japanese	6·36	2·01	0·76	2·89	49·43	38·55
Silverhull	6·41	1·78	0·53	3·06	52·09	36·13
Tartary	7·85	1·33	0·31	1·93	54·95	33·63

The ash of buckwheat contained: From (1) United States; (2) Mean of Wolff's analyses; K_2O, 35·15, 23·07; Na_2O, 2·26, 6·12; CaO, 6·62, 4·42; MgO, 20·55, 12·42; Fe_2O_3, 1·68, 1·74; P_2O_5, 24·09, 48·67; SO_3, 3·59, 2·11; Cl, 0·67, 1·30; SiO_2, 5·54, 0·23 per cent.

D. G. H.

Corrosion of Metals by Milk. H. A. Trebler, W. A. Wesley and F. L. LaQue. (*Ind. Eng. Chem.*, 1932, 24, 339–350.)—The corrosive action of sweet milk on nickel, copper, nickel-silver, an experimental chromium nickel alloy, and a chromium nickel iron alloy has been investigated. Nickel was found to be only slightly corroded during normal pasteurisation, and the normal increase of corrosion on rise of temperature is prevented by formation of a protective film on the nickel, helped by supersaturation with air and high velocity of the milk. During cooling, the film is not present, and corrosion is appreciable during the first stages, decreasing as the temperature falls, and depending on the usual factors. Supersaturation of the milk with air and high velocity may then operate in the opposite way. Nickel is regarded as suitable for conveying and storing milk at temperatures not above 18° C.; but it should not be used in contact with milk cooling in the range from 63° to 18° C. The addition of sufficient chromium (12 to 15 per cent.) gives an alloy resistant under all conditions to corrosion, and the limited number of tests made on the chromium nickel iron alloy (18 : 8 : 74) indicated that it also would be suitable for milk plants. There was no material film formation on copper, and there is risk of corrosion of copper or nickel-silver in the final stages of heating and the first stages of cooling of milk. Galvanic corrosion was found to be negligible.

D. G. H.

Investigation of the Degree of Heating of Milk. Orla-Jensen. (*Z. Unters. Lebensm.*, 1932, 63, 300–308.)—In the author's "creamometric" method (*Lait*, 1929, 9, Nos. 86–90) the sample is heated for 5 minutes at 50° C., and 5 c.c.

of milk, plus 5 c.c. of water, and 10 c.c. of undiluted milk are placed in suitable (Höyberg or Gerber) cream-butyrometer tubes, and the thickness of the layer of cream is read in each case after 2 hours at 12 to 15° C. Addition of a colouring matter (*e.g.* the Storch reagent) gives a well-defined layer. The agglutinating powers of milk are weakened by heating, and cream-formation is, therefore, delayed. The ratio (*A*), 2 × thickness of cream in dilute milk/thickness in undiluted milk, should exceed 1 for raw milk, and is less than 1 for milk pasteurised at a low temperature. In certain cases (*e.g.* where the undiluted milk gives only a thin layer of cream) the fat content of the undiluted milk is taken as the denominator. This gives a ratio (*C*) which is 3·9 to 10 (mean 8·3) for raw milk, 0·1 to 3·7 (mean 1·3) for permanently-pasteurised milk, and 0 to 0·3 for milk treated by the Stassan process (momentary heating in a thin layer at 75° C.). Full data, tabulated for 30 samples, show that with milk for children (3·9 per cent. of fat), *A* and *C* are reduced, respectively, from 2·5 and 7·4 for unheated milk, to 1·3 and 4·6 after 15 seconds at 70° C., and to zero after 15 seconds at 78° to 80° C.; corresponding figures for full-milk (fat 3·75 per cent.) are 2·1 and 7·7 (raw), 1·5 and 5·3 (70° C.), 0 (76° to 80° C.). The suitability of other methods proposed as indications of the various degrees of heating of milk is discussed. In particular, estimation of amylolytic power, which is destroyed after 0·5 to 1 hour at 53° C., is a suitable indicator of low-temperature pasteurisation; active amylase in such milk may be due to starch-fermenting streptococci in mastitis milk. Since iodine is held by fat and casein, it is preferable in this test to take 10 c.c. of the whey produced from 40 c.c. of milk after 1 hour at 40° C. in the presence of 1 c.c. of 0·25 *N* hydrochloric acid, and to add 5 drops each of a 5 per cent. solution of potassium iodide and 0·1 per cent. hydrogen peroxide; experiments should be made by the author's method (*loc. cit.*), with the use of 3, 5, 7, or 9 drops of 2 per cent. starch solution. J. G.

Gas Storage of Pork and Bacon. Part I. Preliminary Experiments. E. H. Callow. (*J. Soc. Chem. Ind.*, 1932, **51**, 116–119T.)—Pieces of pork and of mild-cured green bacon, weighing 1 lb., were hung in large vacuum desiccators, containing, at different temperatures, pure or commercial nitrogen, pure or commercial carbon dioxide, or air. At 0° C., pork stored in commercial carbon dioxide was in perfect condition after 2 months, and after 70 days tasted better than fresh pork, and there was practically no loss in weight. In air the meat was overgrown with micro-organisms after 17 days, and in nitrogen, although growth of aerobic organisms was prevented, the development of anaerobic organisms was encouraged, so that this gas is useless for this purpose. For mild-cured green bacon nitrogen was found to be nearly as good as carbon dioxide; the storage life was more than doubled at 5° C., and the colour was brighter than that of bacon stored in air, owing to the apparent stability of nitrosohaemoglobin (to which bacon owes its pink colour) in the absence of oxygen. Carbon dioxide had a marked inhibiting effect on the growth of the micro-organisms obtained from pork suffering from aerobic and anaerobic spoilage. Commercial carbon dioxide prevented growth more effectively than nitrogen. At − 1° C. no growth appeared in pure carbon dioxide in 50 days, but it appeared in 25 days in commercial carbon dioxide and in nitrogen (pure and commercial), and in air it appeared in 4 days. D. G. H.

Fruit Juice Rich in Tannin as a Sensitive Reagent for Pectin. C. Griebel. (*Z. Unters. Lebensm.*, 1932, **63**, 291–300.)—The reagent is best prepared from "speierling" (*Pyrus domestica*), but field pear (*P. communis*), service berry, sloe, cornelian cherry, lotus plum, and other fruits may also be used. The ripe fruit is peeled rapidly with a brass knife, and the juice is removed by pressure, boiled, and filtered while hot. As a reagent it is then stable for 2 or more years so long as it is stored in a filled bottle with a narrow neck, and is covered with a layer of toluene 0·5 cm. deep to prevent access of air, and, consequently, fermentation. If it develops a cloudiness it should be diluted with twice its volume of water and, after 12 hours in the ice-chest, it should again be filtered. For the test, 0·2 c.c. is added in small drops to 1 c.c. of the sample in a small test-tube, when 0·1 per cent. of pectin shows a haze developing into a precipitate, whilst 0·01 per cent. appears as an opalescence (no precipitate). By the use of the technique of Uhlenhut's precipitation test, 1γ of pectin is detectable in 0·5 c.c. of liquid, the maximum sensitiveness of the ordinary alcohol reaction being 1:1,000. A blank test should always be made as a precaution. Comparable tests with a number of commercial tans (*e.g.* mangrove, pine-bark, oak-wood, mimosa and quebracho extracts) gave negative reactions, and it is concluded that there is present in the tannin idioblasts another substance which is associated with the tannin, and which is responsible for the precipitation. J. G.

Comparative Study of Juices from Frozen Fruits. T. A. Pickett. (*Ind. Eng. Chem.*, 1932, **24**, 353–354.)—Blackberries, cherries, dewberries, peaches, pears, plums, raspberries, and strawberries were examined fresh, and after slow and quick freezing for varying periods. The juices were expressed, centrifuged, and tested for hydrogen-ion concentration and titratable acidity, and in many cases for the freezing-point depression, conductivity and total solids. The juices from all these fruits, frozen and tested immediately, had greater titratable acidities than the juices from the fresh fruits; apparently this is due to a breaking down or increased permeability of the cells upon freezing. Further, the titratable acidity increases as length of time of storage increases, partly owing to dehydration. Since the juices of fruits frozen and stored at −12·2° C. have greater titratable acidities than those frozen at −73·3° C., and stored at −12·2° C., the juices of the fruits frozen at the lower temperature more nearly resemble the fresh juices in this respect. The freezing-point depression figures follow the same lines as those for the acidities. D. G. H.

Quantitative Determination of Laevulose and Sucrose. J. Fiehe. (*Z. Unters. Lebensm.*, 1932, **63**, 288–291.)—Solutions of various concentrations of a number of sugars were heated for 30 minutes on the water-bath with 10 c.c. of 5 *N* hydrochloric acid (in such a manner as to avoid over-heating), the cooled liquid was diluted to 50 c.c., and 5 c.c. were mixed with 5 c.c. of 32 per cent. hydrochloric acid, and shaken with 30 c.c. of a 0·625 per cent. solution of phloroglucinol in 16 per cent. hydrochloric acid. The resulting hydroxy-methyl-furfural-phloroglucinol compound ($C_{12}H_{10}O_5$) was filtered off after 24 hours, washed with 20 c.c. of water, and weighed after 3 hours at 110° C., and 3 hours in air (*cf.* Fiehe and Kordatzki, ANALYST, 1929, **54**, 241; 1932, **57**, 254). Solutions (1 per cent.)

of dextrose, maltose, lactose, and wheat starch gave a yellow colour, and arabinose a blue-green colour, but no precipitate. Ten c.c. of a 1 per cent. solution and 5 c.c. of 2·3 and 4 per cent. solutions of sucrose yielded 12·36, 12·26, 20·40, and 27·65 mgrms. (means) of precipitate, respectively; 10 c.c. of 0·5 per cent. and 5 c.c. of 1, 1·5 and 2 per cent. solutions of laevulose yielded 11·07, 11·71, 18·70, and 26·65 mgrms., respectively. Results reproducible to within about 0·5 per cent. are obtainable if not less than 11 mgrms. of precipitate are weighed. The results indicate that 50 mgrms. of sucrose correspond with 26·3 mgrms. of laevulose if 10 c.c. of a 1 per cent. solution of the former are taken. The weight of precipitate obtained is not directly proportional to the amount of sugar taken, relatively higher results being obtained for the more concentrated solutions. J. G.

Modification of the Seliwanoff and Ihl-Pechmann Reactions for Laevulose. C. I. Kruisheer. (*Rec. Trav. Chim. Pays-Bas*, 1932, **51**, 273–278.)—These colour reactions are not specific for laevulose, since similar colorations, although of less intensity, are given by dextrose, galactose, lactose, and some other sugars. The disturbing influence of monosaccharides may be removed by oxidising these to the hexonic acids by the action of hypoiodite, eliminating the excess of iodine by adding sodium sulphite, and precipitating the iodides as cuprous iodide. Removal of the influence of disaccharides presents greater difficulty, which has not been entirely overcome. The hypoiodite treatment annuls the free aldehyde group of lactose, maltose, etc., and diminishes the disturbing effect by one-half. Preliminary heating with hydrochloric acid is unsatisfactory, as it not only destroys part of the laevulose, but yields a certain amount of hydroxy-methyl-furfural, which resists the oxidising action of the hypoiodite. The procedure outlined above diminishes not only the disturbance due to carbohydrate other than laevulose, but also that due to other extraneous substances, this being of especial advantage in urine analysis.

With pure sugar solutions, 2 c.c. of the liquid (containing not more than 2 per cent. of sugar) are treated in a 50-c.c. Erlenmeyer flask with 0·5 c.c. of 4 *N* sodium hydroxide solution and 2 c.c. of 0·1 *N* iodine solution [13 grms. of iodine and 15 grms. of potassium iodide to 100 (? 1000) c.c.], and, after 5 minutes, with 4 c.c. of 12 *N* hydrochloric acid and 4 c.c. of copper sulphate solution (25 grms. of $CuSO_4$, $5H_2O$ to 100 c.c.). Sodium sulphite solution (20 grms. of Na_2SO_3, $7H_2O$ to 100 c.c.) is then added until the liquid assumes the cream colour of cuprous iodide, large excess being avoided. The liquid is transferred to a test-tube, and, when the precipitate has settled, 8 to 10 c.c. of the clear or almost clear solution are pipetted off and treated, in a roomy test-tube, with either 10 drops of a 20 per cent. solution of resorcinol in alcohol (Seliwanoff test, *Ber.*, 1887, **20**, 181), or with 10 drops of a 20 per cent. solution of diphenylamine in alcohol (Ihl-Pechmann test, *Chem. News*, 1881, **51**, 114). The vessel is immersed in a boiling water-bath for 15 minutes; the appearance of a red (resorcinol) or blue (diphenylamine) colour indicates the presence of free or combined laevulose. With small amounts of the sugar the colour is rendered more distinct by shaking the cooled liquid with 2 c.c. of pure amyl alcohol or liquid phenol. The diphenylamine test responds to 0·002 per cent. of laevulose, but the resorcinol test is somewhat less sensitive;

both give negative results with 2 per cent. of dextrose, mannose, galactose, xylose, or arabinose.

In the case of urine, 80 c.c. are treated with 30 c.c. of half-basic lead acetate solution, and either centrifuged or left to settle; 25 c.c. of the clear liquid are mixed with 11·5 c.c. of saturated sodium phosphate solution, and again allowed to settle, 1 c.c. of the clear liquid thus obtained being oxidised with hypoiodite, and treated further as described above. Under these conditions, normal urine (with or without 4 per cent. of added dextrose) and diabetic urine (with 1·05 per cent. of dextrose) give no colour reactions, but urine containing 0·05 per cent. of laevulose reacts distinctly, and one with 1 per cent. of lactose just perceptibly. T. H. P.

Origin of Honey Diastase. J. Fiehe. (*Z. Unters. Lebensm.*, 1932, **63**, 329–331.)—The author considers that the diastase in honey is derived principally from the plant juices (*e.g.* the nectar), and, to a less extent, from the bees. This is contrary to the conclusions of certain other workers, but it may explain the low diastatic values obtained as a result of feeding with sugar, and the relatively high values from heather or buckwheat honeys. Hence honey which contains only bee diastase and relatively little plant diastase may sometimes behave like heated honey in the diastase test. Two similar samples of rosemary (*Rosmarinus officinalis*) honey from Narbonne contained 18·95 and 18·35 per cent. of water, and 2·29 and 1·26 per cent. of sucrose; the polarisation readings were − 3·0° and − 1·5° before, and − 3·4° and − 1·72° after inversion. Fiehe's test was negative, and the diastase values were 1·0 and 0, respectively. J. G.

Accidental Presence of Acrolein in Cider "Brandies." G. Warcollier and A. Le Moal. (*Compt. rend.*, 1932, **194**, 1394–1396.)—Brandies obtained by distilling cider or perry are normally free from acrolein, but in those of last season from 0·12 to 1·66 grm., per litre (18·1 to 255·4 grms. per hectolitre of absolute alcohol) was found for cider spirit, and 0·625 grm. per litre (86·0) for perry spirit. The acrolein may be formed from the glycerol by the action of *B. amaracrylus*, which occurs in water and causes bitterness in wines, or of organisms of the *B. Welchii* group. Acrolein is detected by means of: (1) Codeine, which gives a transient green coloration. (2) Voisenet's reaction with acid-albumin, hydrochloric and nitrous acids, which give a green coloration with from 0·1 to 1 mgrm. of acrolein per litre. This reaction fails if the proportion of acrolein is high, or if much acetaldehyde is present. (3) Arnold and Mentzel's reaction with phenylhydrazine hydrochloride and ferric chloride, which give a red colour with acetaldehyde or a green colour with acrolein (not less than 1 mgrm.). Normally, cider and perry spirits contain only traces of acetaldehyde, and the red colour rapidly gives way to the green if acrolein is present. (4) If the ferric chloride of reaction (3) is omitted, a green colour of intensity proportional to the acrolein content appears after 12 to 24 hours. (5) The Schiff–Gayon reaction. This may be made specific for acrolein if applied to a solution rich in sulphuric acid. To 5 c.c. of solution containing at least 2 mgrms. of acrolein are added 5 c.c. of sulphuric acid (dilution 1+1), the tube being shaken under cold water. Addition of 4 c.c. of Schiff–Gayon reagent then yields a persistent, apple-green coloration, which gives quantitative results when compared with solutions containing 1 to 10 grms. of acrolein per 1000 of 95 per cent. (by vol.) alcohol. T. H. P.

Fatty Acids and Component Glycerides of some Oleo Oils. A. Banks and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1932, **51**, 111–116T.)—Three North American oleo oils from three centres of production were analysed, and an examination of the glyceride structure showed that the fully-saturated components of the oleo oils are richer in palmitic and myristic acids than those of the original tallows. Whilst the oleo oils, as a whole, contain more palmitic (with myristic) acid, the total amount of stearic, oleic and linolic acids (68–70 mols. per cent.) is much the same as in many tallows. The proportions of palmitic (with myristic) acid (30 mols. per cent.), and of the total C_{18} acids (about 70 mols. per cent.) in the not fully saturated components of the oleo oils are very similar to those for the same class of glycerides in the tallows themselves, suggesting the approach to constancy of the not fully saturated glycerides of cattle-storage fats. These results are to be expected as a result of pressing the whole fats, which will leave behind the glycerides of higher melting point, in which stearic acid will predominate, although a lower melting-point component will exert solvent power on a closely-related derivative of higher melting-point, so that, in practice, no quantitative separation will occur. D. G. H.

Solubility of Vanillin and Coumarin. R. M. Hitchens. (*Ind. Eng. Chem.*, 1932, **24**, 418–419.)—The solubility of vanillin in cold dilute ethyl alcohol is low, but it rises rapidly with increase in the alcohol concentration and the temperature. With 70 per cent. alcohol the solubility is 76·7 grms. per 100 c.c. of solution at 40° C. Vanillin melts under ethyl alcohol at 50° C. Coumarin is much less soluble in ethyl alcohol solutions. Vanillin is not very soluble in glycerol solutions, and the solubility does not rise suddenly with increase of glycerol concentration and temperature. The highest value obtained was 11·4 grms. per 100 c.c. of solution; the maximum solubility of coumarin in glycerol solution was found to be 1·68 grms. per 100 c.c. W. P. S.

Existence and Distribution of Caffeine and Theobromine in Guarana. G. Bertrand and P. de Berredo Carneiro. (*Bull. Soc. Chim.*, 1932, **51-52**, 284–288.)—An examination of the seeds, leaves, roots, stems and buds of guarana (*Paullinia cupana*) has been made, particularly with reference to the proportions of caffeine and theobromine. The seeds consisted of 83·5 per cent. of kernel, containing: water, 11·02; fatty extract, 2·68; ash, 2·07; and caffeine, 3·91 per cent. No theobromine was found either in the kernels or in paste made from kernels. The following results are calculated on the dry material:

		Theobromine Per Cent.	Caffeine Per Cent.
Seeds		—	3·91
Leaves		1·20	0·38
Roots	Central cylinder	—	0·27
	Bark	—	1·74
Stems	Wood	—	0·19
	Bark	0·98	0·17
Buds	Flowers	1·54	—
	Flower stalks	0·38	

Both theobromine and caffeine are regarded as being formed in the leaves and in the green cells of the stem bark. In the flowers the degree of methylation of the xanthine does not proceed further than the formation of theobromine, and, once formed, both theobromine and caffeine may be translocated, but the slighter solubility of the theobromine may partly account for its less general distribution. The presence of both substances in the leaves is significant, seeing that caffeine only is present in tea, maté, coffee, *Ilex cassine*, and the leaves of *Neea theifera*.

D. G. H.

Detection of Diacetyl and Methyl-Acetyl Carbinol in Foodstuffs, etc. H. Schmalfuss and H. Barthmeyer. (*Z. Unters. Lebensm.*, 1932, **63**, 283–288.)—The authors' method (*Z. physiol. Chem.*, 1928, **176**, 282; *Biochem. Z.*, 1929, **216**, 330) is applied as follows:—*Diacetyl.*—Tobacco (3 grms.) is burned in a clay pipe, and the vapours are drawn through two wash-bottles containing 3 c.c. of 10 per cent. sulphuric acid. The resulting liquid is then mixed with 0·33 c.c. of 20 per cent. hydroxylamine hydrochloride and 0·2 c.c. of 1·27 per cent. nickel sulphate $(+7H_2O)$ solutions, and 25 per cent. ammonia is added until the liquid is slightly alkaline. It is then heated for 1 minute and cooled, and the red nickel dioximine (Tschugaeff, *Z. anorg. Chem.*, 1905, **46**, 144) is removed by filtration and washed with a little alcohol and weighed; 0·26 grm. (of nickel dioximine) was obtained from 1 kilo. of tobacco. Coffee is ground and shaken with 500 c.c. of saturated salt solution in a 1500-c.c. flask, and the contents are heated, at a temperature which is increased gradually from 110° to 150° C., in a current of carbon dioxide. Two 50-c.c. portions are collected and saturated with salt, and the process is repeated, the final distillate (8 c.c.) being treated as described; 60 grms. of Costa Rica coffee yielded 1·1 mgrm. One kilo. of Dutch cocoa and 4 litres of dark beer each yielded 1·2 mgrm.; 5 litres of milk, soured with *S. acidi lactici* and *S. cremoris*, 2·1 mgrms.; 1 kilo. of butter, 0·1 to 0·6 mgrm.; and 5 kilos. of heather honey, 0·1 mgrm. of precipitate (m.pt. 232·5 to 236° C., according to the source).

Methyl-acetyl Carbinol.—Fifty c.c. of the residue after distillation are treated with 50 c.c. of 50 per cent. ferric chloride solution in order to convert the methyl-acetyl carbinol into diacetyl, which is determined as before. In all cases allowance is made for any blank. Deposits from the fermentation of cane and grape sugar with bakers' yeast, China tea, and black bread, gave negative results. J. G.

Rapid Method for the Determination of Nicotine in Unfermented Tobacco. O. Dafert and M. T. Bollbecher. (*Z. Unters. Lebensm.*, 1932, **63**, 331–333.)—The tobacco is dried and powdered, and 2 grms. are shaken well for 2 hours in a dry 50-c.c. stoppered flask with 2 c.c. of sodium carbonate solution (strength not stated), 40 grms. of trichloroethylene, and a little talc. The mixture is then filtered through a dry paper and ammonia is removed from 30 grms. of the filtrate (=1·5 grm. of tobacco) by a passage of a current of air for 2 minutes, the solvent being then removed from the residual liquid by slow evaporation in the presence of 10 c.c. of 0·1 *N* sulphuric acid. When the odour is no longer apparent, water is added to the residue to make a volume of 10 c.c., the liquid is filtered (to remove chlorophyll and resinous substances), and the nicotine is determined by means of an immersion-refractometer calibrated against a solution containing 0·1 per cent. of pure nicotine sulphate and pure 0·1 *N* sulphuric acid. The maximum errors for 0·76 to 5 per cent. of nicotine (on the air-dried sample) are ±0·05 per cent. (compared with Shedd's method). The method of Bodnár, Straub and Nagy (*Biochem. Z.*, 1928, **195**, 103; 1929, **206**, 410) gives high results, and that of Brezina (*Chem. Zentr.*, 1917, I, 700) is also unreliable. J. G.

Removal of Nicotine from Tobacco Smoke. J. Traube. (*Chem. Ztg.*, 1932, **29**, 287.)—Absorption of nicotine and other poisons from tobacco smoke is effected by introducing a sufficiently thick layer of silica gel into the mouthpiece of the pipe or the holder of cigar or cigarette. Nicotine has a strong effect in lowering surface tension. With a stalagmometer the drop number was found to be 42·0 for water, and 47·6 for a 0·16 per cent. solution of nicotine. The efficiency of silica gel in removing nicotine from smoke has been demonstrated by passing the smoke through water, with and without the use of silica gel, and then testing the drop number. Without silica gel the drop number rose to 56, but, with it, was only 45 after the smoke from ten cigarettes had been passed through it.

R. F. I.

Determination of Nitroglycerin in Drug Preparations (Acid Distillation Method). E. L. Anderson. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 140–145.)—Colorimetric methods for this determination are unsatisfactory, and the ether extraction method, which has been in use during the past two years, has not given good results. The alcohol aliquot method will give high results if other alcohol-soluble nitrogenous constituents are present. The method now described is based on the volatility of nitroglycerin with steam, as it is distilled directly from a slightly acid solution of the sample into an alkaline solution, in which it is saponified. It is then reduced with Devarda's alloy, and the resulting ammonia is distilled into standard acid solution. Difficulty was experienced with this second distillation. When a Murray scrubber (*J. Amer. Pharm. Assoc.*, 1924, **13**, 423) was used as a trap in the neck of the distillation flask, blank experiments gave distillates requiring from 0·5 to 1·5 c.c. of 0·02 *N* sulphuric acid for neutralisation. These volumes were reduced to 0·1 to 0·5 c.c. by inserting, as a second trap, a 300-c.c. Kjeldahl flask containing 25 to 30 c.c. of water, and surmounted by a third trap of the type used in Kjeldahl distillations; the water in this Kjeldahl flask trap was kept heated during the distillation of the ammonia.

Sufficient of the tablets or solution to represent 0·05 grm. of nitroglycerin is mixed in an 800-c.c. Kjeldahl flask with 50 c.c. of saturated sodium sulphate solution (to raise the boiling point and prevent charring), 150 c.c. of water, and enough 10 per cent. sulphuric acid (5 to 10 drops) to give an acid reaction to litmus. This is distilled, through a trap and condenser, into an 800-c.c. Kjeldahl flask containing 30 c.c. of 5 per cent. sodium hydroxide solution, into which the outlet tube dips; a medium flame is used until the air is expelled, and then a large flame, the distillation occupying about 1 hour. The condenser is then washed with about 100 c.c. of water into the collecting flask. After addition of 2 grms. of Devarda alloy, the ammonia is distilled into 25 c.c. of 0·02 *N* sulphuric acid; 1 c.c. of this acid≡0·001514 grm. of nitroglycerin. This procedure gives good results, provided that great care is given to the details of the operations. T. H. P.

Behaviour and Identification of Arecoline and its Use as a Taenicide, with some Comparisons with Pelletierine. C. D. Howard. (*Amer. J. Pharm.*, 1932, **104**, 170–175.)—Arecoline is the active alkaloid of the areca nut, and the dosage for tapeworm in dogs is variously given as 1 to 16 mgrms., whilst the dose for pelletierine tannate (from pomegranate root-bark) is about 0·3 to 0·4 grm. One ⅛ grain tablet of arecoline, administered to a guinea-pig of 350 grm. in weight, caused, in 5 minutes, paralysis of the rear limbs, but after half-an-hour recovery began. The administration of 1¼ tablets (10 mgrms.), however, on 3 occasions, caused death in 5 hours, after preliminary apparent recovery. Arecoline and pelletierine preparations resemble one another in many respects, but they may be distinguished by the smaller dose of the former, and the fact that it is usually met with as the hydrobromide, whilst pelletierine is used as the tannate; also by the odour of pelletierine base on distillation, the readier and more distinctive crystallisation of arecoline salts from alcohol and chloroform, the failure of picric acid to precipitate arecoline in dilute solution, and the more pronounced myotic action of arecoline. Moreover, sulphuric and selenious acids give a deep rose-red colour with pelletierine, deepening on heating, and eventually changing to a dirty olive-green, whilst with arecoline a bright yellow colour results. The melting-point of arecoline hydrobromide (anhydrous needle-shaped prisms or plates) is 167°–168° C., and that of pelletierine picrate is 150° C. Further reactions of arecoline and pelletierine include the following:—With potassium bismuthous iodide a crimson precipitate in faintly acid solution, and a distinct turbidity in 1 in 20,000 solutions. Iodine in potassium iodide (Wagner's reagent) is next in sensitiveness, the limit being 1 in 5,000 for arecoline, and 1 in 10,000 for pelletierine. Mayer's reagent is not so sensitive, and phosphomolybdic acid gives a greenish-white precipitate with a 1 in 1000 arecoline solution. No precipitates are obtained with mercuric chloride, platinic chloride, auric chloride, tannic acid, lead acetate or lead subacetate in moderately dilute solution. D. G. H.

Reaction for Distinguishing Primary Cyclic Amines and its Application to Medicines. J. A. Sanchez. (*Ann. Chim. anal.*, 1932, 14, 152.)—Primary cyclic amines may be distinguished from primary, secondary or tertiary fatty amines by the colour reaction with a furfural acetic reagent, prepared by adding glacial acetic acid to a saturated solution of furfural in cold water, in the proportion of 5 drops of acid to 100 c.c. of furfural. For a free amine 1 or 2 drops of furfural reagent are added to 1 drop of the liquid amine or to a few mgrms. of the solid, when a bright eosin-red or violet-red colour develops on mixing, and, if no colour is apparent, 1 drop of concentrated hydrochloric acid is added, since it intensifies the colour. With amines in combination, dissociation must first be brought about by hydrolysis, so that to 0·05 grm. of the amine are added 2 drops of 30 per cent. sodium hydroxide solution, and the mixture is heated until evaporated to dryness or until dense aromatic fumes appear, and, after cooling, 1 drop of furfural reagent and 1 drop of concentrated hydrochloric are added. The red or violet-red colour at once forms, giving an alcoholic solution of the same colour. The amine function may thus be demonstrated in such substances as antifebrin, phenacetin, stibenyl, lactophenin, etc. Novocaine and tutocaine may be distinguished from stovaine, or cocaine from alipine. Similarly, atoxyl and arsenobenzenes may be identified. D. G. H.

Determination of Aluminium in Organic Materials. G. J. Cox, E. W. Schwartze, R. H. Mann, and R. B. Unangst. (*Ind. Eng. Chem.*, 1932, **24**, 403–405.)—A suitable quantity of the organic material is dried and incinerated at the lowest possible temperature, the ash is treated with water and hydrochloric acid, evaporated to dryness and, after the addition of hydrochloric acid and water, the silica is separated by centrifugal action. The liquid is decanted, 1 c.c. of nitric acid and 1 c.c. of 0·1 *M* ferric sulphate solution are added, and the mixture is evaporated to about 10 c.c., diluted with water to 60 c.c., and treated with 5 c.c. of 1 *M* mono-sodium phosphate solution and 2 c.c. of 0·04 per cent. bromophenol blue solution. Ammonia (7 *M*) is added until a permanent precipitate is formed, the *p*H is adjusted to 4·2 by the addition of 3 *M* sodium acetate solution, and the mixture is centrifuged. The liquid portion is discarded, and the precipitate is dissolved in 0·5 c.c. of 6 *M* hydrochloric acid, 1·25 c.c. of glacial acetic acid and 15 c.c. of hot water. Five c.c. of 6 *M* sodium hydroxide are added, the mixture is centrifuged, and the liquid is decanted through a double filter. [If two filter papers are used, the filtrate will not give a reaction for iron when tested with mercaptoacetic acid (thioglycollic acid) and ammonia]. After the precipitate has been washed with hot water the filtrate and washings are diluted to 100 c.c. Twenty c.c. of this solution are treated with 25 c.c. of a solution containing 1 grm.-mol. of ammonium acetate, 1 grm.-mol. of ammonium chloride, 80 c.c. of 0·1 per cent. ammonium aurin tricarboxylate solution and 60 c.c. of 6 *M* hydrochloric acid per litre; the mixture is boiled under a reflux condenser for one minute, cooled, sufficient 1·6 *M* ammonium carbonate solution (4·8 to 5 c.c.) is added to give a final *p*H of 7·1, the mixture is shaken to expel carbon dioxide, and, after twenty minutes, the coloration is compared with that of a solution containing 5 c.c. of 0·04 per cent. thymol blue solution and 8 c.c. of 6 *M* hydrochloric acid per 500 c.c. The amount of aluminium present is determined by reference to a curve plotted from the colorimetric readings obtained when various quantities of aluminium are subjected to the entire scheme of analysis, beginning with the ash.

W. P. S.

Aluminium Content of Foodstuffs Cooked in Glass and in Aluminium. G. D. Beal, R. B. Unangst, H. B. Wigman and G. J. Cox. (*Ind. Eng. Chem.*, 1932, **24**, 405–407.)—Foods were cooked in glass (Pyrex) and in aluminium, and the average increases in the amounts of aluminium were determined (see preceding abstract). A negligible amount is taken up by neutral foods; acid and alkaline foods have more action. In no case is sufficient aluminium dissolved from utensils to interfere seriously with phosphorus absorption in an animal consuming the food. An average daily human intake of aluminium, when all foods are cooked in aluminium, is estimated at 12 mgrms., of which about 5 mgrms. are derived from the utensils. The increase in aluminium content varies from *nil* in potatoes boiled whole in their skins to 49 parts per million in apricots cooked for 40 minutes. The largest amount was 118 parts per million in "apple butter," which had been cooked for 6½ hours in an aluminium vessel. A selection of other figures is as follows:—*Oatmeal*, cooked for 150 minutes in a glass vessel, a content of 1·48 parts per million of aluminium, and cooked in aluminium 8·8 p.p.m.; *creamed cabbage*, cooked for 45 minutes in glass, contained 0·37 p.p.m., and in aluminium 2·78 p.p.m., but, when cooked with sodium carbonate, there was an increase of 90·5 p.p.m. *Orange marmalade*, cooked for 90 minutes, in glass, gave 0·3 p.p.m., and in aluminium 3·06 p.p.m. *Cranberry sauce*, cooked for 10 minutes with sugar in glass, gave 0·6, and in aluminium 3·2 parts per million, but in aluminium without sugar 7·9 p.p.m. *Fried bacon*, cooked 5 minutes in glass, gave 0·25, and in aluminium 0·68 part per million. J. W. B.

Biochemical

Determination of Glutamine in the Presence of Asparagine. A. C. Chibnall and R. G. Westall. (*Biochem. J.*, 1932, **26**, 122–132.)—Attention is called to the fact, previously discovered by Schulze and Bosshard (*Landw. Versuchs-Stat.*, 1883, **29**, 305) and Thierfelder and von Cramm (*Z. Physiol. Chem.*, 1919, **105**, 58), that glutamine reacts abnormally with nitrous acid. It gives 92 per cent. of its total nitrogen as amino-nitrogen in the Van Slyke apparatus. The stability of glutamine in solution at 100° C. at various *p*H values has been investigated by determinations of both the amide-nitrogen and the amino-nitrogen. After being heated at 100° C. at *p*H 8 for 3 hours, glutamine gives 35 per cent. of the total nitrogen as amide-nitrogen, whilst the amino-nitrogen falls to 8·5 per cent. Asparagine is stable under these conditions. This difference in behaviour has been made the basis of a method for the separate determination of asparagine and glutamine in plant extracts. The method has been applied with success to a mixture of asparagine and glutamine, and also to six plant extracts, the amide contents of which were known from the previous work of Schulze. After investigation for possible sources of error, and bearing in mind the limit of accuracy with which the amino-nitrogen of a plant extract can be determined, it is recommended that the glutamine and asparagine content of a plant extract should be determined as follows:—(1) Glutamine amide-nitrogen + asparagine amide-nitrogen = increase in amide-nitrogen with *N* sulphuric acid. (2) Glutamine amide-nitrogen = increase in amide-nitrogen at *p*H 8 × 1·4. (3) Asparagine amide-nitrogen = (1)–(2). (4) The ratio "decrease in amino-nitrogen/increase in amide-nitrogen" at *p*H 8 should be about 2·3. (5) The ratio "glutamine amide-nitrogen/decrease in amino-nitrogen with *N* sulphuric acid" should be about 1. It will be raised if peptide-splitting occurs during the hydrolysis. (6) The presence of urea can be detected by an increase in the value of (2) if determined at *p*H 4. (7) The small error due to allantoin falls almost entirely on the value for asparagine amide-nitrogen. The instability of glutamine in aqueous solution offers an explanation of the low yields of crystalline glutamine obtained by Schulze from plant extracts. P. H. P.

Bromine Reaction of Pregnancy Urine. A. R. Armstrong and E. Walker. (*Biochem. J.*, 1932, **26**, 143–146.)—Voge (*Brit. Med. J.*, 1929, **2**, 829) suggested that Knoop's test for histidine, when applied to urine, offered a simple test for pregnancy. Knoop's test consists in the addition of bromine water to the solution under examination to the point of maximum absorption, avoiding excess. On heating, a port wine-red colour develops, and fades slowly, on standing, and a black particulate precipitate is deposited. The reaction works best in faintly acid solution; the colour is modified, but not inhibited, by the presence of strong acids. The question arose whether the substance causing the reaction was histidine, as is always assumed. Therefore the authors have now isolated the substance in pregnancy urine which gives a positive reaction with bromine water (Knoop's test), and have identified it as histidine. No other substance has been found by them to give a Knoop reaction similar to that of histidine, and the only substance quoted in the literature is that of methylhistidine by Linneweh, Keil and Hoppe-Seyler (*Z. physiol. Chem.*, 1929, **183**, 11). The methylhistidine of Fargher and Pyman (*J. Chem. Soc.*, 1921, **119**, 734) does not give a positive Knoop test, but in this case the methyl group is attached to the amino-group, whereas in Linneweh, Keil and Hoppe-Seyler's methylhistidine the methyl group is attached to the ring. Therefore Knoop's test is considered to be specific for histidine and *N*-methylhistidine. P. H. P.

Milk Peroxidase. Its Preparation, Properties and Action with Hydrogen Peroxide on Metabolites. K. A. C. Elliott. (*Biochem. J.*, 1932, **26**, 10–24.)—It is generally believed that peroxidases are almost universally present in the tissues of animals and widely distributed in plants and bacteria, but it has not yet been shown experimentally that they serve any physiological function. It is even doubted whether their specific oxidising substrate, hydrogen peroxide, ever occurs significantly in normal living matter, but it is certain that hydrogen peroxide is formed by certain oxidising systems separated from living matter; it seems likely that hydrogen peroxide could be a normal tissue product. It was felt that more knowledge of the powers of peroxidase with hydrogen peroxide as an oxidising agent for substances of metabolic interest might throw light on its possibilities in a biological mechanism, and a study has been made to see what possible metabolites can be oxidised by hydrogen peroxide and an animal peroxidase under more or less physiological conditions. The separation of milk peroxidase by fractional precipitation with ammonium sulphate is described, whereby a crude, but considerably concentrated, preparation is obtained practically free from catalase. The activity of the preparation degenerates very slowly in the refrigerator at 0 to 5° C. (in 6½ months the activity of one sample dropped from a "purpurogallin number" of 3·6 to 2·4). The enzyme is active from about *p*H 4 to nearly *p*H 10. A colour appears to be associated with the enzyme, and haemochromogen bands can be obtained. Compounds which contain the –SH group, such as cysteine, glutathione and denatured proteins, interfere with tests for peroxidase with benzidine, guaiacum, and, to some extent, with *p*-phenylenediamine. This appears not to be an inhibition of the enzyme, as with hydrogen sulphide, but seems to be due to the reduction of the coloured reaction products by –SH compounds. A method for the determination of hydrogen peroxide in very small amounts (1 mgrm. in 35 c.c.), by the measurement of the evolution of oxygen by manganese dioxide, is described. The volume of gas obtained is affected by the presence of proteins, phosphate, acid, etc., but in given conditions it is proportional to the hydrogen peroxide initially present. Conditions were devised by which nitrite could be oxidised quantitatively by hydrogen peroxide with peroxidase, as shown by the consumption of hydrogen peroxide and the disappearance of nitrite. Under similar conditions tyrosine and tryptophane were found to be oxidised to coloured products. Under the conditions in which nitrite is quantitatively oxidised no oxidation by hydrogen peroxide and peroxidase of the following substances was obtained: Formate, acetate, oleate, stearate, triolein, ethyl alcohol, glucose, glycerol, acetaldehyde, β-hydroxybutyrate, lactate, glycine, phenylalanine and histidine. Dihydroxyacetone and phenylglyoxal are oxidised by very dilute hydrogen peroxide without peroxidase. Thus the attempt to find any general activity of the system which might throw light on the physiological function of peroxidase has failed. Possibly the enzyme from milk may differ fundamentally from peroxidases found in active tissues, but this seems unlikely, since it is a very active enzyme, and will oxidise all the substances which are used in the ordinary qualitative tests for other animal peroxidases, and, in general, seems likely to have the same properties as they have. It is thought that it would be premature to suggest pigment-formation as a function of the enzyme. A study of the powers of a vegetable peroxidase as a catalyst of oxidations by hydrogen peroxide is now in progress. P. H. P.

Vitamin *A* and Carotene. IX. Conversion of Carotene into Vitamin *A* in the Cow. T. Moore. (*Biochem. J.*, 1932, **26**, 1–9.)—It has previously been shown that carotene, or some part of it, suffers conversion in the rat into the colourless vitamin *A*. The degree of yellow pigmentation of the body-fat of animals varies considerably between different species; thus the rat, sheep and pig possess colourless body-fats, whilst man, the ox and the fowl have more or less pigmented fats. It seemed desirable to examine the fate of carotene in animals of the latter group before reaching any conclusion as to the general applicability of results obtained with the rat. Both carotene and vitamin *A* have been shown to be present in the unsaponifiable fraction of New Zealand butter-fat, and, whereas the feeding of cows on carrots or green stuff leads to increases both in the carotene content and vitamin *A* activity of the butter-fat, the administration of cod-liver oil results only in increased vitamin *A* activity, and the degree of yellow pigmentation remains unchanged. These observations, which first seemed to support the view that no relation could exist between carotene and the vitamin, might now seem to point to an incomplete conversion of carotene in the cow, or even to an interchangeability of the functions of the pigment and vitamin in this animal. In the hope of shedding light on this question, two main lines of investigation have been followed:—(1) Specimens of liver, butter, etc., obtained from different cows, have been examined by the colorimetric method for carotene and vitamin *A*, and a comparison of specimens obtained from Jersey cows with those from other breeds has been made, since the Jersey cow is reputed to show unusually deep pigmentation in its body- and milk-fat. (2) The effects of giving carotene in the food, as carrots or red palm oil, have been studied on the degree of pigmentation and vitamin *A* content of butter-fat obtained from a cow at the end of the winter stall-feeding period. The results show that, although the body-fat of the cow is normally characterised by the presence of small amounts of carotene, vitamin *A*, as such, is present in preponderating amounts, in both the liver-fat and the milk-fat. Since the cow is purely herbivorous, this finding suggests that carotene undergoes the conversion into vitamin *A* previously demonstrated in the rat. The conclusion is supported by the finding that the feeding of a cow with carotene, in the form of carrots, at the end of the winter stall-feeding period resulted in an increase, not only in the carotene content, but also in the vitamin *A* content of the butter-fat. The degree of pigmentation of butter-fat, when adequate carotene is available in the diet, is determined by breed. Butter-fat derived from Jersey cows gave a yellow value twice that obtained with butter-fat from Shorthorn cows under similar nutritive conditions. When the cow is at pasture the output of carotene and vitamin *A* in the butter-fat is very small in comparison with the amount of carotene available in the diet. Storage of vitamin *A* in the liver takes place, and a large excess of pigment must undoubtedly be excreted unchanged. It is noteworthy that, just as in the rat, the vitamin *A* content of the body-fat remains within normal limits in the face of large dietary excess of carotene, so in the cow the vitamin *A* and carotene of the butter-fat are maintained at normal values under similar conditions. On the other hand, during stall-feeding upon a diet almost devoid of carotene, the reserves of vitamin *A* available in the liver and elsewhere may be insufficient to meet the demands of prolonged lactation. In practical dairying a small allowance of carrots, or other material rich in carotene, should suffice to restore a positive balance. P. H. P.

Reduction Capacity of Plant Foodstuffs and its Relation to Vitamin *C*. III. Content of Reducing Substance in Different Fruits and Vegetables. J. Tillmans, P. Hirsch and J. Jackisch. (*Z. Unters. Lebensm.*, 1932, **63**, 241–267.)—The authors' method (ANALYST, 1932, **57**, 260) has been applied to about 130 samples of various fruits, vegetables, juices, preserves, and tinned foodstuffs, and the results are tabulated for extracts of the sample in a four-fold volume of cold water, or in 2 to 3 per cent. sulphuric acid, for 24 hours, and also at the b.pt. in the same solvents for 4 minutes. In some cases it was necessary to shake the liquid with a little nitrobenzene and to centrifuge the mixture, in order to remove most of the colour. In general, the hot sulphuric acid extracts gave the maximum titration values with the indicator, and these were closely parallel to the vitamin *C* values obtained from animal experiments recorded in the literature (Scheunert, *Der Vitamingehalt der Deutschen Nahrungsmittel*, 1929; Berg, *Die Vitamine*, 1927). Exceptions (*e.g.* with preserves or tinned foods) were traced to soluble metallic salts, but the high values from leaf vegetables do not appear to be due to the presence of any reducing substances other than those associated with vitamin *C*. Titration of the fresh extract with 0·001 *N* sodium thiosulphate solution 1 minute after the addition of an excess of 0·001 *N* iodine solution, in the presence of starch, gave values showing, as a rule, a close relationship with those obtained with the oxidation-reduction indicator. This method, however, is less specific, and the results are often high, particularly with old extracts. For the purposes of comparison the expression $10T/A$ was used, where T is the maximum number of c.c. of 0·001 N indicator equivalent to 10 grms. of sample, and A is Hahn's guinea-pig unit (cf. *Z. Unters. Lebensm.*, 1931, **61**, 369, 545). The samples are classified as follows, according to the values of T:—Eight hundred to 100 c.c., parsley, green cabbage, Brussels sprouts, horseradish, kohlrabi and black currant; 100 to 50 c.c., chives, orange, lemon, elderberry, mountain ash, strawberry, red cabbage, mangold, cauliflower, green pea; 50 to 20 c.c., banana, blackberry, grapefruit, raspberry, red and white currants, mandarin, haw, gooseberry, spinach, white cabbage, leek, asparagus, tomato, turnip, radish, potato; 20 to 10 c.c., apple, bilberry, sweet and acid cherry, cranberry, quince, greengage, peach, plum, head lettuce, green bean, bayberry, melon, pumpkin, cucumber, beet; 10 to 1 c.c., apple, apricot, pear, dried fig, grapes, rhubarb, pickled cucumber, carrot, comfrey, celery, sugar beet, onion (*cf.* following abstract).

J. G.

Reduction Capacity of Plant Foodstuffs and its Relation to Vitamin *C*. IV. Reversibility of the Oxidation of the Reducing Substances in Lemon Juice. J. Tillmans, P. Hirsch and H. Dick. (*Z. Unters. Lebensm.*, 1932, **63**, 267–275.)—It is shown that the first stage of the oxidation of the reducing substances responsible for the vitamin *C* content of lemon juice (cf. *id.*, 1932, **63**, 1, 12, 21; Szent-Györgyi, *Biochem. J.*, 1928, **22**, 1387, and preceding abstract) is reversible. This oxidation may be carried out by means of 2·6-dichlorophenol-indophenol; by the passage of a stream of atmospheric oxygen for 3 hours at room-temperature, or for a shorter period at higher temperature; by the action of an equivalent amount of hydrogen peroxide for a few minutes in a boiling solution (its action for 1 hour at 0° and 25° C., respectively, produces only 5 and 50 per cent. of this effect); chlorine and iodine (*loc. cit.*) are also effective. Oxidation by air is irreversible, but the effects of the other reagents may be reversed if a stream of hydrogen sulphide is passed through the neutral or weakly acid solution for 5 minutes at 25° C., and the gas is allowed to remain in contact with the liquid in a stoppered flask for 24 hours, and the excess then removed in a current of nitrogen; the reversal is incomplete after oxidation with chlorine. Palladium-hydrogen is less effective, and in all cases the juices should be fresh, and prolonged contact with the oxidising agent should be avoided if it is required to restore the full reduction titration value (T). The results are supported by experiments on animals.

J. G.

Vitamin *C* Content of Orange Crush Beverage. E. M. Koch. (*Ind. Eng. Chem.*, 1932, **24**, 351–352.)—Orange crush is made by pressing fresh oranges and adding to the thick mixture of juice, pulp and some skin, sugar, lemon citric acid, small amounts of preservative, and a colour, storing the mixture at refrigerator temperature, and finally diluting a week's supply with tap or carbonated tap water. Oranges stored at refrigerator temperature were found to retain their vitamin *C* for at least 3 months; orange juice, unstrained, loses its antiscorbutic potency so rapidly that a test extending over 4 weeks shows a loss, and in 3 months destruction appears to be almost complete; a heavy crush syrup made from the juice unstrained, by adding sugar and preservative and acidifying with lemon citric acid, retains the vitamin as satisfactorily as the original fruit, but this syrup, when diluted to 12 volumes with water, again rapidly loses its antiscorbutic properties. When the dilution of the crush was made in the laboratory with a minimum exposure to air and at room temperature, there was no detectable loss of antiscorbutic potency after storing for 10 days, so that a maximum interval of 10 to 14 days between dilution and consumption of the finished product assures the presence of antiscorbutic properties. It appears that the vitamin of the original juice is preserved by the high acidity and possibly by the high sugar content of the syrup. D. G. H.

Vitamin *D* Content of Red Palm Oil. W. J. Dann. (*Biochem. J.*, 1932, **26**, 151–154.)—A brief description is given of the fruits of the oil palms from which red palm oil is obtained. Four different samples of red palm oil, of which one was a native-rendered oil, whereas the others were "plantation oils" rendered by machinery in plantation factories, have been examined for their vitamin *D* content by the preventive method on albino rats. All four specimens were found to contain very little vitamin *D*. The richest of the four oils used (the native red palm oil) contained less than one-thirtieth as much vitamin *D* as an ordinary cod-liver oil. The red palm oils and cod-liver oils are, however, almost alike in their vitamin *A* activity. Therefore, the use is recommended of red palm oil as a convenient source of vitamin *A* free from vitamin *D* in nutritional experiments, and it appears likely that any sample of red palm oil, preferably of deep colour (*i.e.* particularly rich in carotene), having a low free fatty acid content (*i.e.* a plantation oil), could be used with safety. The native method of preparation of the oil involves its exposure in the open for long periods. If the palm fruit contains ergosterol, irradiation by the tropical sun might well transform a small amount of ergosterol into vitamin *D*, and thus native oils, in general, would be likely to contain more vitamin *D* than plantation oils. P. H. P.

Bacteriological

Growth of *Aspergillus versicolor* on Higher Paraffins. S. J. Hopkins and A. C. Chibnall. (*Biochem. J.*, 1932, **26**, 133–142.)—A mould has been found which will grow on synthetic higher paraffins as sole source of carbon. It is best described at the present time as a strain of *Aspergillus versicolor* (Buillemin) Tiraboschi. Its action on certain synthetic long-chain paraffins has been investigated, in the hope that information would be gained as to the manner in which the organism attacks a long carbon chain of this type, which has no polar group. The mould will grow on both odd- and even-number paraffins, but not on those with a longer chain than $C_{34}H_{70}$; it was only with great difficulty that growth could be obtained on *n*-tetratriacontane, $C_{34}H_{70}$. In experiments to find out the way in which the paraffin chain is attacked by the mould, a large scale culture on *n*-heptacosane, $C_{27}H_{56}$, did not yield any products of metabolism except carbon dioxide and mould mycelium. Indirect evidence has, however, been obtained from experiments with higher ketones on which the mould grew vigorously, and with secondary alcohols on which no growth was obtained at all. It appears that the primary product of oxidation of a paraffin is a ketone or polyketone, and that further oxidation results in the production of shorter-chain fatty acids, which are then metabolised in the usual way. The scheme of metabolism excludes the initial formation of secondary or polyhydric alcohols, and in this respect only does it differ from the air oxidation of paraffins observed by Francis *et al.* (*J. Chem. Soc.*, 1922, **121**, 496; 2804). It is, of course, highly improbable that the paraffin chain could be oxidised at the terminal carbon atom, with the formation of a primary alcohol or *n*-fatty acid containing the same number of carbon atoms. P. H. P.

Effect of Carbon Dioxide on Bacterial Growth, with Special Reference to the Preservation of Fish. Part I. F. P. Coyne. (*J. Soc. Chem. Ind.*, 1932, **51**, 119–121T.)—Bacterial growth and autolysis chiefly account for the deterioration of fresh fish, and a study of the action of bacteria has been begun. Stock cultures were plated out on to horse heart agar, and single colony transfers were made into broth after incubation for 4 days at room temperature. Broth cultures were incubated for 3 days at room temperature, after which one loopful (platinum wire loop, 4 mm. diameter) was inoculated on to each plate, to be tested by making 7 successive strokes across the surface of the agar. Plates were tested in air, in hydrogen, in carbon dioxide, and in nitrogen. *Achromobacter*, *Flavobacter*, *Micrococcus*, *Bacillus* and *Pseudomonas* sp. all showed marked inhibition of growth in carbon dioxide, and the first three could not grow in strictly anaerobic conditions (hydrogen). Neither lack of oxygen nor *p*H value appears to account for the result, and further work is being carried out to establish the theoretical basis for the effect. The organisms inhibited by carbon dioxide are those which predominate in the normal bacterial flora of fish. D. G. H.

Agricultural

Evaluation of Sulphur Suspensions used in Spraying. R. M. Woodman. (*J. Soc. Chem. Ind.*, 1932, **51**, 103–107T.)—The methods of analysis of sulphur suspensions are examined, particular attention being given to the determination of total solids, total sulphur, and non-combined sulphur. The properties which a good sulphur suspension should possess are discussed. With many commercial suspensions the following determinations give useful results. *Total Solids.*—A portion of a well-shaken sample is weighed in a tared, well-stoppered weighing bottle, and evaporated to dryness at 100° C. *Total Sulphur.*—This is determined by the Hodsman's bomb method (*J. Soc. Chem. Ind.*, 1931, **50**, 391T) on 0·05 to 0·1 grm. of the dried residue powdered to pass a 100-mesh sieve. *Free Sulphur.* (*a*) *Carbon Disulphide Extraction Method.*—One to 2 grms. of the dried residue are extracted with several successive portions of 10 c.c. of carbon disulphide, the sulphur in the extract after evaporation of the solvent being finally dried at 100° C. This simple extraction method is not applicable to sulphur suspensions which contain protective colloid (*e.g.* "Sulsol" suspension), since the protective colloid prevents the sulphur from being quantitatively dissolved. The following modified extraction method was used for "Sulsol," acetone being used to coagulate the suspension: 10 c.c. of acetone were shaken with 10 c.c. of a diluted "Sulsol" suspension. After allowing 3 hours for sedimentation of coagulated solids, the mixture was shaken with 20 c.c. of carbon disulphide, kept overnight, and the carbon disulphide layer was run off. Extraction with a further 20 c.c. of solvent was made, 3 or 4 days being allowed for the emulsion to "break" completely. The combined extracts were washed with water, the carbon disulphide was allowed to evaporate spontaneously, and the residue of sulphur was weighed after drying at 100° C. *Free Sulphur.* (*b*) *"Polysulphide" Method* (applicable to all sulphur suspensions).—Twenty-five c.c. of a diluted suspension (the total solids being less than 0·25 grm.) are mixed with 35 c.c. of sodium sulphite solution (10 per cent.), and heated on a water-bath for 45 minutes, with shaking every 10 minutes; 30 c.c. of strontium chloride solution (10 per cent.) are added, the liquid is filtered after 10 minutes, and the precipitate is well washed with boiling water until the filtrate amounts to nearly 300 c.c. An aliquot part of the filtrate, containing the sulphur as thiosulphate, is titrated with 0·05 *N* iodine solution. A correction for any thiosulphate originally present in the suspension is made by a method similar to the A.O.A.C. method (*A.O.A.C. Methods*, 1920, p. 68): 50 c.c. of the diluted suspension are mixed with 20 c.c. of ammoniacal zinc chloride solution, diluted to 300 c.c., thoroughly shaken, and kept overnight; the liquid is filtered, and an aliquot part titrated with 0·05 *N* iodine solution after neutralising with tartaric acid to methyl red indicator. The rate of sedimentation of three commercial sulphur suspensions was measured by determining the free sulphur in portions of the liquid withdrawn at different depths from a column of the suspension after a 22-hour period of sedimentation. S. G. C.

Determination of Minute Amounts of Boron in Soils. W. W. Scott and S. K. Webb. (*Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 180–181.)—The following adaptation of published methods is described. *Separation of the Boron.*—One hundred grms. of soil (dried at 105° C.) are digested in 100 c.c. of boiling water, and the liquid is filtered. A small quantity of sodium carbonate is added to the filtrate, which is then evaporated to 25 c.c., transferred to a platinum dish, and evaporated to dryness, and the residue is ignited. The cooled residue is treated with 10 c.c. of phosphoric acid, and the contents of the dish are transferred, with the aid of 20 c.c. of methyl alcohol, to a 250-c.c. distilling flask fitted with a water-cooled condenser. The liquid is distilled from a water-bath, and the distillate is collected in a platinum dish. Ten c.c. of methyl alcohol are added to the flask, and the distillation is continued. Four to 6 drops of *N* sodium carbonate solution are added to the distillate, which is concentrated to 5 c.c., transferred to a small platinum crucible (25 to 30 c.c. capacity), and evaporated to dryness. *Colorimetric Determination.*—To the residue, 4 drops of concentrated hydrochloric acid and 0·5 c.c. of water are added, the solution is transferred to a small glass vial (30 mm. high), and diluted to 2 c.c. A strip of turmeric paper (45 × 3 mm.) is immersed in the liquid to a depth of 15 mm., and allowed to soak for 3 hours at 35° C. or, preferably, 24 hours at room temperature. The height (in mm.) of the red stain thus produced on the paper is compared with that of stains similarly produced by known amounts of boron in the form of boric acid. This method is suitable for determining 0·005 to 0·1 mgrm. of boron oxide; larger vials and longer strips of turmeric paper are required for amounts in the range 0·1 to 1·0 mgrm.

S. G. C.

Loss of Toxicity of Pyrethrum Dusts. F. Tattersfield. (*J. Agric. Sci.*, 1932, **22**, 396.)—The loss of toxicity of pyrethrum dusts on exposure to light and air is shown to be due to oxidation, and is greater with dusts than with powdered flower heads. The dusts were prepared by extracting the flowers with petroleum spirit and evaporating, the residue being taken up with absorbent earths. The toxicity was tested biologically, the bean aphis being used as a test subject. The loss of toxicity was tested, both biologically and by determining the ferricyanide reducing value, after exposure in thin layers under varying conditions. It was found that both light and air were necessary to cause loss; exposure to inert gases or *in vacuo* caused very little loss. Certain anti-oxidant compounds were found effective in protecting pyrethrum dusts against loss of toxicity on exposure. A dust to which 5 per cent. of hydroquinone had been added preserved its activity for 13 days, and even 1 per cent. had a definite effect. Colloidal sulphur and paraldehyde gave no protection. The following anti-oxidants were tested after being added to the dusts in the proportion of 2·5 per cent.:—Tannic acid, pyrocatechol, resorcinol and pyrogallol afforded a high degree of protection, whereas phenol and phloroglucinol gave little or none. Myrobalans and cutch powders gave some protection.

It appears that the superior stability of powdered pyrethrum flowers over dusts is due not to the presence of a stabiliser, but mainly to the larger size of the particles, or to the active principles being contained as cellular inclusions. R. F. I.

Water Analysis

Zinc in Water Supplies. E. Bartow and O. M. Weigle. (*Ind. Eng. Chem.*, 1932, **24**, 463–465.)—Some of the water supplies in the Missouri-Kansas-Oklahoma district contain up to 50 parts per million of zinc, but, although no ill effects have been observed in persons drinking these waters, it is suggested that a limit of 5 parts per million should remain the standard for drinking water.

W. P. S.

Organic Analysis

Use of Sinalbin as an Indicator. K. Harrison. (*Biochem. J.*, 1932, **26**, 88–89.)—Sinalbin, the glucoside of white mustard seed (*Sinapis alba*, Boiss.), may be used as an indicator. As shown by Will (*J. Pharm. Chim.*, 1872, 327), it develops an intense yellow colour with alkalis, which disappears on addition of excess of acid. For its preparation 400 grms. of the finely-ground seeds are extracted with carbon disulphide in a large Soxhlet apparatus until the extract is free from the yellow essential oil. The residue (200 grms.) is dried in air, and boiled for 30 minutes with 500 c.c. of 95 per cent. alcohol to inactivate enzymes; the alcoholic liquid is filtered hot, and, on cooling (preferably in ice-water), the glucoside crystallises out. A second extraction with hot alcohol gives a further yield. The crystals are filtered off, washed with a little ether, and twice re-crystallised from hot 98 per cent. alcohol; yield 4–5 grms. The stock indicator solution is of 0·5 per cent. strength; solutions in dilute (30 per cent.) alcohol keep indefinitely, whereas aqueous solutions are liable to attack by moulds. The *p*H range is 6·2 (colourless) to 8·4 (yellow); the salt and protein errors are small. Sinalbin is suitable for the titration of weak acids and bases, and may be used with ammonia. It is affected by carbon dioxide in the cold, but may be used for the determination of carbonates in boiling solution; the carbonate must be run into a known excess of hot acid, and not *vice versa.* It should be useful for the micro-titration of some alkaloids, particularly quinine. P. H. P.

Vieböck and Schwappach Method for the Determination of Methoxyl and Ethoxyl Groups. E. P. Clark. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 136–140.)—Zeisel's method has certain limitations. The gravimetric determination of silver iodide involved occupies much time, and, if the material to be analysed or the reagents used contain sulphur, the silver nitrate solution must be replaced by pyridine, which is washed from the receivers when the reaction is completed. The solution is then evaporated to dryness, and the residue is dissolved in water and treated with silver nitrate. This procedure is, moreover, applicable only to methoxyl groups.

A volumetric method for determining methoxyl and ethoxyl groups, which is free from the above objectionable features, particularly the interference of sulphur, has been given by Vieböck and Schwappach (see Hans Meyer, *Analyse und Konstitutionsermittlung,* 5th Edit., 487), which the author now modifies in some details. The procedure follows Zeisel's method, except that the alkyl iodide is collected in an acetic acid solution of potassium acetate containing a little bromine. The following reactions then occur: $CH_3I + Br_2 \longrightarrow CH_3Br + IBr$ and $IBr + 2Br_2 + 3H_2O \longrightarrow HIO_3 + 5HBr$. The solution containing the iodic acid is washed into a flask containing a little sodium acetate, the excess of bromine is removed by means of formic acid, potassium iodide is added, the solution is acidified with sulphuric acid, and the iodine liberated is titrated with 0·1 *N* thiosulphate solution. As six atoms of iodine are liberated for each OCH_3 group, 1 c.c. of the thiosulphate is equivalent to about 0·5 mgrm. of methoxyl, so that 20 to 30 mgrms. of substance are ample for a macro determination. Micro determinations may be made in the same way with about 5 mgrms. of substance, 0·02 *N* thiosulphate being then used for titrating the iodine. Full details of the procedure and a dimensioned sketch of the apparatus used are given. Test analyses gave with α-methylglucoside (4·8 mgrms.) 15·9 (calculated 15·98) per cent. of OCH_3, and with monoacetyldihydrotoxicarol (5·44 mgrms.) 12·5 (calc. 12·5) per cent. T. H. P.

Determination of Methoxyl, Lignin and Cellulose in Plant Materials. M. Phillips. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 118–131.)—Brief summaries are given of the literature dealing with these determinations. For methoxyl, the modification of the Zeisel and Fanto apparatus (*Z. anal. Chem.*, 1903, **42**, 554) recommended is described, and the procedure followed is given in detail.

For lignin, the method used is that depending on dissolving the cellulose and other carbohydrates by means of fuming hydrochloric acid and weighing the residual lignin. An apparatus is described in which two separate 1-grm. samples of the material, previously extracted with a mixture of 32 parts of 95 per cent.

alcohol and 68 parts of benzene, and dried, are treated side by side with the acid. After the two residues of crude lignin have been dried and weighed, one of them is incinerated and the ash weighed; in the other the nitrogen-content is determined by the Kjeldahl method. Then, lignin = crude lignin − ash − (nitrogen × 6·25).

For determining the cellulose, use is made of the chlorine-treatment method. Two 1-grm. samples of the extracted and dried material are weighed in fritted glass crucibles, the weighings being made in weighing bottles. One of the crucibles is then fitted to a filter flask, and washed through with water, chlorine (water-scrubbed) being then passed through the crucible for 5 minutes, at the rate of one bubble per second. The material is next washed with dilute sulphurous acid, followed by water. The crucible is then placed in a 250-c.c. beaker filled with 2 per cent. sodium sulphite solution to within one-half inch of the top of the crucible, and the beaker is left on a steam-bath for 30 minutes. The second crucible is treated similarly, each being then washed with water under suction, and again chlorinated and digested with sodium sulphite solution. This procedure is repeated until the chlorinated material no longer gives the reddish-violet reaction of lignin chloride with sodium sulphite solution. Finally, the cellulose in the crucibles is bleached by adding 20 c.c. of 0·1 per cent. potassium permanganate solution, leaving at room temperature for 10 minutes, and rendering colourless with dilute sulphurous acid. It is then washed, successively, with very dilute ammonia solution, hot water, 95 per cent. alcohol, and ether, dried at 105° C., and weighed. On a weighed portion of the final product the ash is determined. The ash-free cellulose, thus determined, is reported as "Cross and Bevan cellulose." In some cases the pentosans in this cellulose are determined by the furfural method, cellulose less pentosans being returned as "pure cellulose." The assumption that all the furfural is derived from pentosans is not, however, justified. T. H. P.

Heat Test applied to Cotton and Linen Fabrics. M. Fort. (*J. Soc. Dyers and Colourists*, 1932, **48**, 94.)—This test is a rapid method for ascertaining whether the tendering of a material is due to acid treatment or to oxidation, where laundering, mercerising, or alkali boiling has removed not only the tendering agent, but also most of the degradation products. It consists in subjecting the fabric to dry heat in a small air-oven containing a white tile mounted on insulating supports on an upper shelf. The cuttings of fabrics are placed on the tile, and observations are made as to their rate of browning when compared with standard samples. The rate of heating the oven is from cold to 200° C. in 10 to 15 minutes. If acid is present on a fabric, browning may set in at 150° to 175° C. The test is also of value when only very small samples are available, *e.g.* those from damaged spots. R. F. I.

Inorganic Analysis

Determination of (Minute Amounts of) Copper. L. C. Hurd and J. S. Chambers. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 236–238.)—Clarke and Jones described (ANALYST, 1929, **54**, 333) a new colour reaction of copper, in which a "permanganate" colour (sensitive to 1 part of copper in 10,000,000 parts of water) is produced when ammonium persulphate and a trace of silver nitrate are added to a very dilute feebly alkaline solution of a cupric salt containing dimethylglyoxime. The various factors contributing to the development of the colour and the use of the reaction for quantitative colorimetric purposes have been exhaustively studied. For satisfactory results it is necessary to adhere closely to the original directions. The colour produced is almost identical with that of a dilute permanganate solution. Since the original statement that the colour shows a tendency to fade on keeping was confirmed, the authors favour for the colorimetric comparison a series of secondary standards of potassium permanganate, with which the colour produced by the unknown quantity of copper can be rapidly compared. The relationship between the copper present and the number of c.c. of $N/500$ potassium permanganate solution present in the standard comparison solution required to match exactly the copper colour has been established, and is shown in graphical form. Sodium sulphate, magnesium sulphate, calcium sulphate, and potassium nitrate in a concentration of 2 mgrms. per c.c. do not appreciably affect the intensity or stability of the colour, but the chloride content should not exceed 0·5γ per c.c. Iron and cobalt (in concentration of 2γ and 0·02γ per c.c., respectively) interfere. S. G. C.

Determination of Lead in Rocks. G. v. Hevesy and R. Hobbie. (*Z. anal. Chem.*, 1932, **88**, 1–6.)—The finely-powdered rock (30 to 40 grms.) was treated with hydrofluoric and sulphuric acids in a gold basin until silica had been removed. To the residue was added a minute amount of radium *D* (an isotope of lead), the activity of which had been determined electroscopically. The radium *D* acts as an indicator for the completeness of the lead recovery, the activity of the lead after isolation being measured and a suitable correction applied, since the percentage recovery of the lead and that of radium *D* must be identical. The acid mass was diluted to 1500 c.c., the insoluble alkaline-earth sulphates collected and converted into carbonates by fusion with alkali carbonate, and the carbonates dissolved in acetic acid. The acetate solution and the original filtrate from the sulphates were treated separately with dilute silver sulphate solution, so as to contain 1 mgrm. Ag per 100 c.c., and precipitated hot with a slow current of hydrogen sulphide, which was maintained until the liquors were cold. The small sulphide precipitates were collected, united, and dissolved in nitric acid, the solution evaporated to dryness, the residue dissolved in 0·001 *N* nitric acid (20 c.c.), and the solution electrolysed for 20 minutes, a little urea being added. The anode (platinum wire 0·6 mm. in diameter) was heated before and after electrolysis at 250° C. and weighed on a micro-balance. For activity measurements the lead peroxide was dissolved in acetic acid, the solution evaporated to dryness on a watch-glass, and the residue tested in the electroscope. The activity of the added solution of radium *D* was measured under the same conditions. The average lead content of 222 different rock samples was found to be 0·0016 per cent.

W. R. S.

Internal Indicator for the Dichromate Titration of Iron. M. E. Weeks. (*Ind. Eng. Chem., Anal. Edit.*, 1932, **4**, 127–128.)—A 1 per cent. solution of *o*-bisanisidine in glacial acetic acid was applied as internal indicator in the usual procedure for the determination of ferrous iron by dichromate (stannous chloride reduction), with satisfactory results. After reduction (one drop in excess of reducing agent), the solution was diluted with 400 c.c. of ice-cold distilled water, and treated with 12 c.c. of mixed concentrated phosphoric and sulphuric acids (1 : 1), 10 drops of indicator, and 30 c.c. of saturated mercuric chloride solution. The titration was carried out without delay, the end-point being reddish-brown. After a few minutes a blood-red colour develops. W. R. S.

New Colorimetric Method for the Detection and Determination of Chromium. G. C. Spencer. (*Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 245–246.)—The test depends on the action of chromic acid in changing the crimson colour of wool dyed with Serichrome Blue R (Schultz, "Farbstofftabellen," 1914, dye No. 164) to a navy-blue shade, and is claimed to be suitable for detecting and determining in a semi-quantitative manner 0·01 to 0·1 mgrm. of chromium (as chromate) in 50 c.c. The dyed wool is prepared by shaking 2 grms. of woollen yarn or flock in a solution of 0·1 grm. of sodium sulphate, and 0·02 grm. of sulphuric acid in 40 c.c. of water, adding 20 c.c. of a solution of 100 mgrms. of the dye in 200 c.c. of water, and heating the mixture on a steam-bath for 30 minutes, after which the wool is filtered off, washed and dried. A number of colour standards are prepared by digesting on a steam-bath for 30 minutes 0·1 grm. of the dyed wool in 50 c.c. of water containing 3 c.c. of *N* sulphuric acid and a known amount of chromium added as a standard solution of potassium dichromate (1 mgrm. of chromium per c.c.), and subsequently filtering off, washing and drying the wool, and mounting it on a spot-plate with adhesive. In testing for chromium, this is separated, together with aluminium and iron, by precipitation as hydroxide. The precipitate is filtered off, washed, digested for 30 minutes in 30 c.c. of water containing 3 c.c. of *N* sodium hydroxide and 5 c.c. of hydrogen peroxide (U.S.P.), and the liquid is then heated until the peroxide is decomposed. The liquid is filtered, and to the filtrate (containing the chromium), 3 c.c. of *N* sulphuric acid and 0·1 grm. of the dyed wool are added. After digesting on a steam-bath for 30 minutes, the wool is filtered off, washed, and dried. The quantity of chromium present can be judged by comparison with the colour standards. Small quantities of tungstic, vanadic, and permanganic acids, ferrous sulphate, manganous sulphate, and chrome alum were found to cause no colour-change of the dye. S. G. C.

Detection of Beryllium in Rocks. G. Rienäcker. (*Z. anal. Chem.*, 1932, **88**, 29–38.)—The sensitiveness of Fischer's reaction with 1, 2, 5, 8-tetrahydroxyanthraquinone (ANALYST, 1928, **53**, 303) was confirmed. The following procedure was worked out for the detection and approximate determination of beryllia in rocks: 0·1 grm. of the finely powdered is fused with 1 grm. of sodium hydroxide for 5 to 10 minutes in an iron crucible. When cold, the crucible is cooled in ice, and the melt dissolved in water, ice being used to prevent the temperature from rising sufficiently to cause hydrolysis of the sodium beryllate. The liquid is filtered and the precipitate washed, the total bulk being 30 c.c. The filtrate, or an aliquot part, is adjusted with dilute sulphuric acid to about 0·33 *N* alkalinity, and treated with 12 drops of the reagent (0·01 per cent. solution in 96 per cent. alcohol). By repeating the test with decreasing aliquot parts of filtrate until the limit of sensitiveness of the reaction has been reached (3 to 5μ grm. in 15 c.c.), the original beryllium concentration can be estimated. The method of decomposition employed ensures removal of the magnesia with the ferric hydroxide. The time required is about 45 minutes. W. R. S.

Separation of Beryllium from Aluminium by Guanidine Carbonate. A. Jílek and J. Kota. (*Z. anal. Chem.*, 1932, **87**, 422–437.)—Aluminium solutions are precipitated by guanidine carbonate; the precipitate is soluble in excess of reagent. The beryllium precipitate is insoluble in excess. In a solution containing ammonium tartrate, guanidine carbonate precipitates beryllium, but no aluminium. The weakly acid chloride solution, containing not more than 0·1 grm. of either oxide, is treated with 50 c.c. of ammonium tartrate solution (21·25 grms. of tartaric acid neutralised with ammonia and made up to 1 litre), and dilute potassium hydroxide solution till it is barely acid to methyl red. It is then stirred and treated at ordinary temperature with 150 c.c. of a filtered 4 per cent. solution of the reagent and 2·5 c.c. of 40 per cent., almost neutral, formaldehyde. The volume is made up to 250 c.c. The crystalline precipitate, which shows a silky lustre, is set aside for 12 to 14 hours, then collected, and washed with a solution containing 50 c.c. of the ammonium tartrate, 150 c.c. of the guanidine, and 2·5 c.c. of the formaldehyde, reagent. It is converted into and weighed as BeO, after ignition to constant weight. W. R. S.

Rapid Determination of Molybdenum in Steel. E. Bertrand. (*Bull. Soc. Chim. Belg.*, 1932, **41**, 98–103.)—Yellow *hydrated* tungstic acid is transferred by means of a pad of cotton wool to strips of filter paper (2 × 12 cm.), which are gently rubbed with the pad until covered with a uniform layer of the tungsten compound. Stannous chloride solution is made from 20 grms. of tin and 200 c.c. of strong hydrochloric acid; the solution is diluted to a litre. If a drop of dilute molybdenum solution is deposited on the prepared paper, and the spot treated with stannous chloride solution, a greyish-blue stain is obtained, the intensity and rate of production of this being proportional to the molybdenum concentration. The sensitiveness is stated to be 0·00005 mgrm. Mo in a drop of solution. The common acids and the metals met with in steel do not interfere; phosphoric acid bleaches the colour to some extent. Copper gives a stain, but this is much less intense; thus, 0·2 per cent. Mo can be detected in copper. The test is applied to steels in the following manner: one grm. is dissolved in 30 c.c. of warm hydrochloric acid (1:1), containing 25 c.c. of phosphoric acid per litre. The addition of phosphoric acid prevents the formation of insoluble tungstic acid. When dissolved, the iron is oxidised with 15 c.c. of 5 per cent. potassium chlorate solution. Chlorine is boiled off; the solution is diluted to 75 c.c., cooled, and made up to 100 c.c. A drop is placed on the test paper, which is then treated with stannous chloride. The stain is matched against others produced by steels of known molybdenum content. A colorimetric scale is prepared from ammonium molybdate solution (1·84 grms. per litre; 1 c.c. = 0·001 grm. Mo). Quantities of 0·25, 0·5, 1·0, 1·5, etc., c.c. are evaporated to dryness, and 1 grm. of steel free from molybdenum is added to each standard. The metal is dissolved, and the solutions are diluted to 100 c.c., as described above. The standard solutions, which are stable, are kept in reagent bottles provided with perforated rubber stoppers; each stopper holds a glass rod, with which a drop of solution is taken. The drops of standard and assay solution are placed on the same strip of paper so as to be wetted at the same time when the tin solution is poured on. The steel used as a standard should, if possible, be similar in composition to that under examination. W. R. S.

Volumetric Determination of Molybdenum with Permanganate. E. Carrière and R. Lautié. (*Comptes rend.*, 1932, **194**, 1167–1168.)—Potassium molybdate (0·5 grm.) is dissolved in 150 c.c. of 18 per cent. sulphuric acid, and the solution reduced under carbon dioxide with 15 grms. of pure zinc wire at 50° to 60° C. The cooled liquid is filtered through zinc wool in an atmosphere of carbon dioxide into a conical flask and titrated with permanganate (3·15 grms. per litre). The results indicate reduction to Mo_2O_3. The degree of reduction remains unchanged if the amount of zinc and acid is increased. A higher acid: zinc ratio causes slightly stronger reduction, a deficiency in zinc incomplete reduction. Hydrochloric acid used instead of sulphuric gives less concordant results. W. R. S.

Determination of Vanadium in Alloy Steels. H. H. Willard and P. Young. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 187–190.)—*Chromium-Vanadium Steels.*—Four to 5 grms. of the steel are dissolved in hot dilute sulphuric acid (30 to 40 c.c. of water with 1·5 c.c. of concentrated sulphuric acid for each 1 grm. of steel, and 2 c.c. in excess), the solution is oxidised with nitric acid, boiled to expel nitrogen oxides, and cooled. Thirty c.c. of phosphoric acid (sp.gr. 1·37) are added, the liquid is diluted to 300 c.c., and an excess of 0·1 *N* permanganate solution (as shown by the pink colour of the solution persisting for 2 minutes) is added. Five c.c. of 0·1 *N* sodium azide solution are added, the liquid is boiled vigorously for 10 minutes, cooled, and 15 grms. of sodium acetate crystals are added (the addition of a few drops of sulphuric acid will be necessary if a permanent precipitate forms); 0·6 c.c. of diphenylbenzidine indicator solution (prepared by dissolving 0·1 grm. of diphenylbenzidine in 10 c.c. of concentrated sulphuric acid, and diluting with 90 c.c. of glacial acetic acid) is added, the solution is kept for 5 minutes to allow the blue colour to develop, and then titrated with 0·025 *N* ferrous sulphate solution until the indicator is discharged. A very sharp end-point is claimed. A correction to be applied for the indicator, amounting to 0·03 c.c. of the ferrous sulphate solution for each 0·1 c.c. of indicator, is *added* to the volume of ferrous sulphate used.

Steels containing Tungsten.—A modification of the above method is necessary when tungsten is present. Tungstic acid is kept in solution as a complex fluoride throughout the analysis. Twenty-five c.c. of water and 4 c.c. of concentrated sulphuric acid are added to a 1-grm. sample of the steel contained in a 400-c.c. beaker; the liquid is warmed gently until the steel is completely decomposed and the tungsten has separated as a black powder; 5 or 6 drops of concentrated nitric acid are then added, a swirling motion is imparted to the contents of the beaker, and 5 c.c. of hydrofluoric acid (48 per cent.), followed by 5 c.c. of nitric acid are added. A clear solution should thus be obtained; this is diluted to approximately 100 c.c., and boiled for 5 minutes, after adding 1 grm. of ammonium persulphate to complete the oxidation of the tungsten. Five c.c. of 0·1 *N* ferrous sulphate solution are added, and the liquid is diluted to between 150 and 175 c.c. and cooled. The vanadium is now oxidised by the addition of an excess of 0·1 *N* permanganate solution. Five c.c. of 0·1 *M* sodium azide solution are added, and the liquid is boiled vigorously for 10 minutes and cooled; 3 c.c. of hydrofluoric acid (48 per cent.) and 0·3 c.c. of diphenylamine sulphonate indicator (prepared by dissolving 3·2 grms. of barium diphenylamine sulphonate in 1 litre of water, adding a slight excess of sodium sulphate, and decanting the clear liquid, which is used as the indicator solution) is added. The colour change of the indicator at the end-point is from purple to green. The correction to be applied for the indicator must be determined by carrying out analyses of a standard steel, the difference between the calculated volume of ferrous sulphate solution required for the known quantity of vanadium present and the volume actually used in the titration, representing the indicator correction to be *added* to the volume of 0·025 *N* ferrous sulphate solution used in the analysis of other steels. S. G. C.

Determination of Sulphur in Coal by the Perchloric Acid Method. G. L. Smith and A. G. Deem. (*Ind. Eng. Chem.*, *Anal. Ed.*, 1932, 4, 227–229.)—The following new method for determining sulphur in coal is described:—To a 1-grm. sample of coal contained in a 300 c.c. Erlenmeyer flask are added 1 grm. of potassium nitrate, 5 c.c. of concentrated nitric acid, 0·16 grm. of ammonium vanadate (to act as a catalyst in the oxidation), 2 to 4 grms. of monochloracetic acid (to prevent subsequent frothing), and 15 c.c. of perchloric acid (70 per cent.). The whole is digested for 10 minutes at 120° C.; the temperature is raised to 180–185° C., and the heating is continued until the coal is oxidised, and an orange-red precipitate of vanadium pentoxide appears (this occurs usually within 10 minutes, but may take 25 minutes). After cooling, 5 to 10 c.c. of concentrated hydrochloric acid are added, and the liquid is heated until the orange-red precipitate is again obtained; 100 c.c. of water and 0·2 grm. of hydroxylamine hydrochloride are added, the liquid is heated to reduce the vanadium to the hypovanadate condition, filtered, and the sulphate in the filtrate, after dilution to 400 c.c., is precipitated by barium chloride in the usual manner. The results of numerous analyses recorded in the paper are low in tendency as compared with the results obtained by the Eschka method. S. G. C.

Determination of Germanium. J. H. Müller and A. Eisner. (*Ind. and Eng. Chem.*, *Anal. Edit.*, 1932, 4, 134–136.)—Germanic sulphide is quantitatively converted into the dioxide by hydrolysis with boiling water, hydrogen sulphide being evolved. Application of the reaction obviates the use of nitric acid for the oxidation of the sulphide, a practice involving risk of loss due to the violence of the oxidation. The sulphide precipitated from 6 *N* sulphuric acid solution under exclusion of air is left in contact with the hydrogen sulphide under a pressure of 2 ft. of water for 12 hours, the flask being connected with the generator. The precipitate is collected in a porous crucible, washed with *N* sulphuric acid, and freed from liquid by suction. The crucible is immersed in sufficient boiling water to cover it, and the liquid is boiled in the covered beaker until the precipitate has entirely dissolved. The crucible is removed and rinsed with water, the solution is concentrated by evaporation, transferred to a tared porcelain crucible, and evaporated to dryness. The residue may be treated with nitric acid for oxidation of traces of free sulphur. It is ignited at 900° C. and weighed as GeO_2.

W. R. S.

Use of Potassium Manganate in Volumetric Analysis. H. Gall and M. Ditt. (*Z. anal. Chem.*, 1932, **87**, 333–338.)—Oxidimetric determinations with permanganate require an acid medium. It is shown that manganate can be applied to oxidimetric work in alkaline media. The manganate solution was prepared according to Gall and Lehmann's directions (*Ber.*, 1927, **60**, 2491; 1928, **61**, 670). The solution is standardised against sodium oxalate. For the determination of phosphorous or hypophosphorous acid the alkaline solution is treated with a distinct excess of manganate solution, and gently boiled for 10 minutes. A known amount of oxalic acid, approximately equivalent to the manganate, is then added, and the solution acidified with 25 per cent. sulphuric acid; the excess oxalic acid is then titrated at 60° C. with manganate. In acid solution the manganate liberates twice as much oxygen as in alkaline solution. W. R. S.

Volumetric Determination of Cobalt with Permanganate. J. Ledrut and L. Hauss. (*Bull. Soc. Chim. Belge*, 1932, **41**, 104–114.)—The precipitation of cobalt oxalate and the volumetric determination of the combined oxalic acid by means of permanganate have been studied. Serviceable results are claimed.

(ABSTRACTOR'S NOTE.—The precipitation of cobalt oxalate as a quantitative method has been adversely criticised, and is not used in standard analytical practice. *Cf.* Grossmann, *Die Bestimmungsmethoden des Nickels und Kobalts*, Stuttgart, 1913.) W. R. S.

Rapid Determination of Sulphur in Brass and Bronze. J. O. Cooney. (*Ind. and Eng. Chem., Anal. Edit.*, 1932, **4**, 33.)—The process is based on solution of the metal in cupric ammonium chloride and determination of the sulphur in the residue. The alloy (5 grms., as finely divided as possible) is digested with the reagent (1 part of the salt, 3 parts water, and acidification with 5 per cent. of hydrochloric acid) at gentle heat, with occasional stirring. When the action is over, the solution is filtered while hot through a sulphur-free asbestos mat under suction. Washing is done with 5 per cent. hydrochloric acid, then with water. The asbestos and residue are returned to the beaker with as little water as possible; an equal volume of strong nitric acid and 10 c.c. of bromine water are added. The action is brought to completion at boiling heat, the bromine is boiled off, and the asbestos is removed by filtration. The filtrate is evaporated to dryness with 0·5 grm. of sodium bicarbonate to dehydrate silica, the residue is dissolved in dilute hydrochloric acid, the solution is filtered, and the filtrate is treated with barium chloride. If lead or antimony is present, it should be precipitated with pure zinc and filtered off with the silica prior to the precipitation of the barium sulphate. W. R. S.

Detection of Nitrous "Oxides" in Sulphuric Acid. L. W. Marrison. (*J. Soc. Chem. Ind.*, 1931, **51**, 110T.)—Two c.c. of the sulphuric acid to be tested are poured into a mixture of 1 c.c. of aqueous sucrose (0·1 per cent.), and 0·5 c.c.

of alcoholic α-naphthol (5 per cent.). The sugar and the α-naphthol will yield a violet ring at the interface of the two liquids. If more than 5 parts per million of N_2O_3 are present in the acid, the lower layer will become green; if more than 0·06 per cent. of N_2O_3 is present, the upper layer will be coloured yellow. The test may be made approximately quantitative by using fresh standards of sodium nitrite in pure sulphuric acid. Nitrites in aqueous solution may be similarly detected by adding 2 c.c. of the solution to be tested to the sucrose-naphthol mixture and pouring in pure sulphuric acid. About 12 parts per million of N_2O_3 are detectable in aqueous solution. Ferrous iron interferes, about 300 parts per million of it giving a fair simulation of 6 parts per million of N_2O_3. Chromic and molybdic acids interfere. The following do not interfere: Chloride, bromide, sulphite, thiosulphate, acetate, borate, perchlorate, phosphate, sulphide, barium, calcium, strontium, copper, cadmium, zinc, mercury, lead, manganese, magnesium.

S. G. C.

Analysis of Nitrous Oxide by Solubility in Water. A. L. Chaney and C. F. Lombard. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 185–187.)—The method is applied to the determination of nitrous oxide in the gas used for anaesthesia, and is a slightly modified form of that described by Bennett (*J. Phys. Chem.*, 1930, **34**, 1137); water saturated with air, nitrogen, or oxygen is used, instead of air-free water, for the absorption of the nitrous oxide, and a correction factor is introduced for the effect of this dissolved gas, instead of employing a graphical method of calculation of the percentage of nitrous oxide. S. G. C.

Microchemical

Carbohydrates. I. Micro-Determination of Carbohydrates in Pure Solutions, and in Animal Material. Z. Dische. (*Mikrochem.*, 1931, **10**, 129–189.)—A comparative description of the different micro methods of sugar determination in use, with complete practical details and references is given. The methods include: A. **Reduction Methods.** 1. *Reduction of Cupric Salts.*—The reduced copper oxide is filtered off, and may be determined titrimetically by dissolving in an oxidising acid reagent and titrating with potassium permanganate, as in the method of Fontes and Thivolle (*Bull. Soc. Chim. biol.*, 1927, **9**, 353). The reduced copper may also be determined iodimetrically by the Shaffer–Hartmann method (*J. Biol. Chem.*, 1920, **45**, 365; Somogyi, *ibid.*, 1926, **70**, 599; and Thompsett, *Biochem. J.*, 1930, **24**, 1148). Alternatively, the unreduced copper may be determined iodimetrically by the MacLean method, modified by Bang (*Biochem. Z.*, 1918, **87**, 248; 1918, **92**, 344), titrating finally with *N*/1000 thiosulphate solution. The reduced copper may also be determined colorimetrically by the Folin–Wu method (*J. Biol. Chem.*, 1919, **38**, 81; **41**, 367; Folin, *ibid.*, 1930, **82**, 83; *ibid.*, 1926, **67**, 357; Benedict, *ibid.*, 1926, **68**, 759; and 1928, **76**, 457).

2. *Reduction of Mercury Salts.*—The method has been worked out on the micro scale for biological material by Baudouin and Lewin (*Bull. Soc. Chim. biol.*, 1927, **9**, 280), and appears to be more rapid and more simple than the copper salt methods.

3. *Reduction of Ferricyanide.*—The reduction of ferricyanide is not so susceptible to back oxidation in the air as the copper salt methods, but is less specific. In the Hagedorn–Jensen method (*Biochem. Z.*, 1923, **135**, 46) the reduced ferricyanide is determined iodimetrically. Flatow (*Biochem. Z.*, 1928, **194**, 132) determines the excess ferricyanide by titrating with 0·2 per cent. indigo carmine solution, and Jonescu (*Bull. Soc. Chim. biol.*, 1928, **10**, 252) determines the reduced ferricyanide by titration with permanganate. The unreduced ferricyanide may be determined colorimetrically by Folin's method (*J. Biol. Chem.*, 1928, **77**, 421; 1929, **81**, 231; 1929, **83**, 115; ANALYST, 1928, **53**, 392; 1929, **54**, 246), or by the method of Van Slyke and Hawkins (*J. Biol. Chem.*, 1929, **84**, 69). The unreduced ferricyanide may also be determined gasometrically by the method of Van Slyke and Hawkins (*J. Biol. Chem.*, 1929, **79**, 739), in which the nitrogen developed by the action of alkaline hydrazine on potassium ferricyanide is measured.

4. *Methods Depending on the Reduction of Organic Substances.*—Chief of these methods is the reduction of acetone-picric acid, in the method of Benedict (*J. Biol. Chem.*, 1929, **48**, 50), and that of Sumner (*ibid.*, 1921, **47**, 5; 1925, **62**, 287; and 1925, **65**, 393). The colour developed is compared with a standard of similar sugar content. In Milroy's method (*Biochem. J.*, 1925, **19**, 746) nitro-anthraquinone sulphonic acid is reduced by the sugar to a red amino compound, in 10 per cent. potassium carbonate solution. Eisenhardt's method (*Münch. med. Wochenschr.*, 1920, p. 1382) depends on the reduction of methylene blue.

B. **Methods Depending on the Fermentation of Sugar.**—Sugar is fermented by yeast and micro-organisms, such as *B. coli*, to carbon dioxide. The method of Wagner (*J. Metabol. Res.*, 1925, **5**, 353) measures, in a Van Slyke apparatus, the carbon dioxide formed, and Grafe and Jorgenfrei (*Deutsch. Arch. klin. Med.*, 1924, **145**, 294), whose method is adapted for blood, use a Barcroft manometer.

C. **Osazone Methods.**—These methods are all colorimetric, and have been used on the micro scale by Dische and Popper (*Biochem. Z.*, 1926, **175**, 371), Dische [*Mikrochem.*, 1929, **1** (Neue Folg.), 1], Glassmann (*Z. physiol. Chem.*, 1925, **150**, 16), and Tillmans and Philippi (*Biochem. Z.*, 1929, **215**, 36).

D. **Methods Depending on Carbohydrate Reactions.**—Methods are based on the characteristic reactions of carbohydrates when heated with different organic substances, such as naphthol, indole, diphenylamine, thymol, phloroglucinol, in concentrated mineral acids. In these methods are also included special methods for determining different carbohydrates in admixture with each other.

II. DETERMINATION OF CARBOHYDRATES IN DIFFERENT ANIMAL MATERIALS.—The application of the methods to various kinds of biological material is discussed in detail, including different methods of removing the protein before the determination. J. W. B.

Micro-Determination of Phosphoric and Arsenic Acids with "Molybdenum-blue." S. Zinzadge. (*Z. für Pflanzenern., Düng. u. Bodenk.*, 1932, **23**, 447–454.)—The method is also described in other Continental journals, *e.g. Ann. agronomiques*, 1931, **43**, 321, *Bull. Soc. Chim.*, 1931, **49**, 872. It depends on the use of a special "molybdenum-blue" reagent, and differs from the existing methods for phosphoric and arsenic acids involving the use of molybdenum compounds in that the reagent and the blue colour produced with these acids are both relatively stable. The reagent can be purchased in a proprietory form from Schering-Kahlbaum, A.G., of Berlin, or the Société des Usines Chimiques Rhône-Poulenc, of Paris, or may be prepared as follows: 120 c.c. of sulphuric acid (sp.gr. 1·785) are well mixed with 6·02 grms. of pure molybdic oxide powder in a porcelain dish; the mixture is heated and stirred until the molybdic oxide is dissolved; after cooling, 70 c.c. of water are added, the liquid is cooled and diluted to 200 c.c. (Solution 1). One hundred c.c. of this solution are boiled for 10 minutes after the addition of 0·28 grms. of pure molybdenum metal powder, cooled and diluted to 100 c.c. (Solution 2). The "molybdenum-blue" reagent is made by mixing solutions 1 and 2 in such a proportion that 2·51 c.c. of the mixture will just decolorise 0·20 ± 0·01 c.c. of 0·1 *N* permanganate solution. *Method.*—One to 30 c.c. of the solution to be tested (containing 0·0005 to 0·5 mgrm. of P_2O_5 or As_2O_5) are placed in a small 50 c.c. conical flask, neutralised with dilute soda solution or sulphuric acid, 2 drops of saturated aqueous 1, 2, 6-dinitrophenol being used as indicator (slight yellow colour at end-point), diluted to 40 c.c., and the "molybdenum-blue" reagent is added. The solution is boiled gently for 5 minutes, kept for a further 15 to 20 minutes, cooled and diluted to 50 c.c. The intensity of the blue colour is compared with that of a standard phosphate solution, prepared from potassium dihydrogen phosphate, which has been treated in the same manner. The quantity of "molybdenum-blue" reagent to be added depends on the amount of phosphate present, and must be established by preliminary trial: for 0·0005 to 0·1 mgrm. of P_2O_5, 0·3 c.c., and for 0·1 to 0·5 mgrm. of P_2O_5, 0·6 c.c., is required. Various colorimeters are recommended for the colorimetric comparison, but for approximate results a colorimeter is not necessary. Arsenic acid reacts with the reagent similarly to phosphoric acid, and may be determined in the same way, a standard comparison solution prepared from arsenic acid being used. Silica does not interfere. S. G. C.

Micro Melting-Point Determinations. H. Linser. (*Mikrochem.*, 1931, 9, 255–268.)—Klein's melting-point apparatus (*Mikrochem. Pregl-Festschrift*, 1929, 192) for the observation of melting points under the microscope is used to determine the temperature of sublimation, melting point, temperature of decomposition and other properties of a number of substances. Before use, a new instrument must be heated several times to 400° C., and maintained at that temperature, so that all the insulating material is thoroughly dried, before reproducible results are obtainable. A calibration curve should be made for each instrument by determining the readings for a number of test substances of known m.pt., when heated at a velocity of 3 to 6° per minute. The m.pt. is taken as the temperature at which the smallest crystals and particles liquefy and the corners of the larger crystals begin to melt. This is not necessarily the same temperature as the macro m.pt. The observed m.pt. is lowered by increasing the velocity of heating. For a number of substances it was found that $y = 3{\cdot}1x$, where x represents melting-point displacement and y the velocity in degrees per minute. Therefore, the velocity of heating should be observed and the correction applied. A further correction table is advisable, in which the corrected value of the melting points of a number of substances is compared with the known value of their melting points. For most instruments this last correction table is redundant, and the true and calculated values coincide. J. W. B.

Reviews

THE NEW CONCEPTIONS OF MATTER. By C. G. DARWIN, M.A., F.R.S. Pp. 192. London: G. Bell & Sons, Ltd. 1931. Price 10s. 6d.

Although Professor Darwin points out that the methods of analytical chemistry —"heating, dissolving and so on—are much too gentle to do more than scrape the surface of the very stable structure of the atom," yet no chemist, be he analytical or of any other variety, can fail to be interested in recent work on the nature of the different atoms with which he is constantly dealing. Professor Darwin's book is the most successful exposition of the new conceptions of matter that has yet appeared. Starting with an admirably lucid description of the behaviour of particles, continuing with an equally straightforward account of the behaviour of waves, it leads on finally to the evidence which proves that electrons, protons and photons all partake of the nature of particles, and yet also all partake of the nature of waves. The reader is led up to this apparent paradox so deftly that he finds himself happily at home among the new conceptions before he has had time to realise the difficulties of crossing from the old, and the present reviewer, at least, is grateful to the author for having exorcised that paralysing inferiority complex which used to inhibit all mental processes when mathematicians or physicists began to talk about 6-dimensional space. D. JORDAN LLOYD.

ANALYTICAL CHEMISTRY. A Textbook for a One-Year Combination Course in Qualitative and Quantitative Analysis. By JOHN C. WARE, Sc.M., Ph.D., Associate Professor of Chemistry, New York University. Pp. xiv+462. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1931. Price 22s. 3d. net.

Judged by the Table of Contents, this is an attractive book, for it comprises in one volume the fundamental physico-chemical facts and theories underlying analytical chemistry (105 pages), qualitative analysis (158 pages), and gravimetric and volumetric methods (157 pages).

Upon closer acquaintance, however, the book proves to be designed for piloting students in American colleges through a one-year's "pre-medical and pre-dental course" in analytical chemistry. Whilst serviceable to those who desire to get through a subsidiary subject with a certain amount of hustle, if necessary, the book can hardly be said to be of general interest to the analytical profession. This is said without intention to criticise the reliability of the text-matter; it is the recurring *Leitmotiv* of cramming that calls for comment. It is "not possible in a one-year course to devote much time, if any, to the non-metals" (p. 243). The chapter on the analysis of solids "should, at least, be carefully read through where there is not sufficient time to make the analyses" (p. 233). In the chapter on the "Colloidal State," it is "not possible to go into details as to what really constitutes the colloidal state," but the student will gather the impression that it constitutes a nuisance which should be prevented rather than studied: "Prevention is better than a cure"; in carrying out a precipitation, "the steps must be followed exactly as given." "Accept your procedure instructions as the accumulated experience of many others." W. R. SCHOELLER.

MICROBES AND ULTRAMICROBES. By A. D. GARDNER, M.A., D.M., F.R.C.S. With an Appendix by G. R. DE BEER, M.A., B.Sc. 21 Illustrations. Monographs on Biological Subjects. London: Methuen. Price 3s. 6d.

There are few analysts who do not, at some time or other, find themselves faced with problems in whose solutions a knowledge of bacteriology must play a part. For some, in the food and agricultural trades, for example, this part will generally be of such importance that they themselves will, in fact, not be expected to tackle the problems, since all the larger organisations will include at least one bacteriologist on their scientific staffs. For others the occasions will be so rare, as in the paint industry or in metallurgical work, that recourse to a library or to the services of a less specialised consultant, will doubtless meet the situation. Intermediate between these two groups stand probably most analytical chemists, including those in general practice, to whom at any moment a general knowledge of the methods of bacteriology and the significance of its results may prove essential.

Bacteriology is, fortunately, a subject whose scope and achievements are quite easy to expound even to a non-technical audience, and, *a fortiori*, to chemists. Its technique, on the other hand, is certainly one of the most exacting in the whole realm of science. For that reason, if for no other, scientists working on subjects adjacent to bacteriology need to know what it does, rather than how it does it, and Dr. Gardner's little book seems ideally suited to telling them. It is clearly written; indeed, it is not exaggerating to say that it is extremely well written, with an attention to the exactness and niceties of scientific prose that is usually all too lacking. It covers the whole general field of bacteriology, with special attention to recent developments in the study of viruses—or ultra-microbes, as the author prefers to call them—and the bacteriophage, the latter at perhaps rather disproportionate length. The fundamental facts in the extremely difficult branch of immunology are also given, and the most recent attempt to place bacteriological classification on a sound taxonomic basis is outlined.

Every chemist, particularly every analytical chemist, who is himself not a trained or practising bacteriologist, would be well advised to read this book. If it does not, and it does not set out to do so, teach him bacteriology, at any rate it shows him where he must submit to be taught. No one can read of the problems involved in ultra-microbiology without a realisation of the extreme technical difficulties involved in their solution; no one is likely to tackle them, or other bacteriological work, after reading Mr. Gardner's book, unless he is satisfied that he has the necessary training and experience.

It is certain, however, that the book will reach a much larger public than the restricted one we have been discussing. Many students will find it a welcome introduction to a frequent subsidiary subject. Consequently, we may be permitted to draw attention to some small defects. The excessive use of diagrammatic illustrations, rather crudely hand-drawn, seems a little out of place in a "Monograph"; occasionally, as in the drawing of *Corynebacterium* (Fig. 2), the effect is so unlike what is actually seen under the microscope as to be actually misleading, but the use of half-tone reproductions of photomicrographs was probably made impossible on economic grounds, because of the low published price of the books in the series.

It would be interesting to learn Dr. Gardner's theories about the facts first made generally known by Besredka, and given by him the most unfortunate and misleading name of "antivirus" phenomena. There is increasing clinical evidence of their importance and quite wide application, and Dr. Gardner goes very near to mentioning them on p. 13, when discussing the possibility that food-exhaustion in a medium can be responsible for the retardation of growth that occurs after the logarithmic phase. If the whole process of culturing, filtering, and sterilisation is repeated a second and a third time, the resulting medium will not support growth of the particular organism that helped to produce it. The dry matter obtained on evaporation of this spent medium can be redissolved to give a medium similarly inhibitory to the relevant organism, and yet able to support the growth of many other species. We can, however, find no explanation of the phenomena in the production by the organism of labile or volatile products toxic to itself.

Attention may, perhaps, be drawn to a few minor blemishes in the author's generally impeccable style; the use of the offensive word "researchers," and of the pointless cliché, "the exception that proves the rule"—especially as the particular exception does not, in fact, prove (that is, *test*) the particular rule—and an over-indulgence in capitals (for example, Hydrogen-ion concentration, p. 41; Mannite, p. 27), might well have been avoided. But, apart from these and an occasional "literal," there are not even minor blemishes to be found in an almost wholly excellent book, a credit alike to author, editor, and publisher.

A. L. BACHARACH.
R. F. HUNWICKE.

QUANTITATIVE ANALYTISCHE MIKROMETHODEN DER ORGANISCHEN CHEMIE IN VERGLEICHENDER DARSTELLUNG. By C. WEYGAND. Pp. 279, with 79 illustrations. Leipzig: Akademische Verlagsgesellschaft, M.B.H. 1931. Price RM. 16, bound RM.18.

The author of a new book on quantitative organic micro-analysis must expect the reader to compare it closely with Pregl's most excellent book on the subject, in order to discover whether the new publication is justified. Professor Weygand has had eight years' experience of teaching and practising micro methods in the University of Leipzig, and has used not only the Pregl methods, but also a number of other micro- and semi-micro methods, which he describes in his book, with critical remarks on each method. Pregl's book, *Quantitative Organic Micro-analysis*, deals, almost exclusively, with his own methods and those worked out in his laboratory, and gives only brief references to other work; therefore, a book which includes, for the first time, a comparative account of all the different micro methods which have developed from the original Pregl methods, is definitely to be welcomed. The new matter not previously in text-book forms occupies approximately one-half of the book.

Professor Weygand, like Pregl, writes with great attention to detail, which is all-important in micro methods, and his book is intended to be read rather than used as a book of reference. One-third of it is taken up with the description of the determination of carbon and hydrogen by the combustion method. The unchanged Pregl procedure is carefully described, without any historical introduction. Among the slight variations in the Pregl method used by different workers, no mention is made of the use of phosphorus pentoxide as a drying agent in the water-absorption tube. The only reference to the use of phosphorus pentoxide is in the description of a recent semi-micro method, in which it is used with sodium hydroxide as the carbon dioxide absorbent; it was, however, used previously, mixed with glass wool, by Drew and Porter (*J. Soc. Chem. Ind.*, 1928, **47**, 17T) with the otherwise unaltered Pregl procedure, and has been found by a number of workers in England, including the reviewer, and also in Germany, to give much more reliable results, at any rate in a humid climate, than calcium chloride, while it has the advantage that the tubes do not need filling so often.

In the description of semi-micro methods of carbon and hydrogen determination no mention is made of the method for the simultaneous determination of carbon, hydrogen and nitrogen by Hackspill and d'Huart (*Bull. Soc. Chim.*, 1924, **35**, 801; ANALYST, 1924, **49**, 447; and *Recent Advances in Analytical Chemistry*, Vol. II, p. 367). Apart from these omissions, the section is admirably complete, and is a reliable guide to the relative importance of the methods.

Useful additions include Van Slyke's method for the determination of amino nitrogen, the new method of Lieb and Krainick for the micro-determination of carbon by the wet method (*cf.* ANALYST, 1932, 273), and the determination of hydroxyl groups by Flaschenträger.

The book is readable, and well printed and illustrated. It is questionable, however, whether some of the photographs are as useful as they are decorative, since they show very simple details of technique. It is to be regretted that Professor Weygand has not, like Pregl, given a calculation for a typical analysis at the end of each description.

The index, like those of many German books, is inadequate, and this makes the work somewhat difficult to use for reference until one is familiar with the whole of its contents. The book is to be recommended to analytical chemists interested in micro methods, not to replace, but to supplement, Pregl's book.

J. W. BROWN.

JULY, 1932 Vol. LVII., No. 676

9. AUG 1932

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, June 1st, the President, Mr. F. W. F. Arnaud, being in the chair.

Certificates were read for the first time in favour of Arthur Littlewood, M.A., A.I.C., and John Henry Weber, B.Sc., A.I.C.

Certificates were read for the second time in favour of Charles Carr Marginson, B.Sc., A.I.C., Ph.C., Wilfred Mather, A.M.C.T., F.I C., Alec Duncan Mitchell, D.Sc., F.I.C., and M. Niyogi, M.Sc.

The following were elected Members of the Society:—Reginald Haydn Hopkins, D.Sc., F.I.C., and William Basil Walker, B.Sc., A.I.C.

The following papers were read and discussed:—"The Determination of Aluminium in Foods," by L. H. Lampitt, D.Sc., F.I.C., and N. D. Sylvester, M.Sc., A.I.C.; "The Spectrographic Determination of Small Quantities of Aluminium," by P. L. Bilham, B.Sc., A.I.C.; and "The Physiological Effects of Aluminium," by J. H. Burn, M.A., M.D.

Notice was given that a Joint Meeting would be held with the Food Group of the Society of Chemical Industry, on the subject of Changes in Fruit on Storage, on Wednesday, October 5th.

Death

With deep regret we record the death, on June 13th, of Mr. Cecil Howard Cribb. An obituary notice will be published in a later issue.

The Determination of Small Amounts of Aluminium in Food

BY L. H. LAMPITT, D.SC., F.I.C., AND N. D. SYLVESTER, M.SC., A.I.C.

WITH A NOTE ON THE SPECTROGRAPHIC METHOD

BY P. BILHAM, B.SC., A.I.C.

(*Read at the Meeting, June* 1, 1932.)

KNOWLEDGE of the effect of small quantities of metals or metallic salts on the human organism is assuming an ever-increasing importance, and it follows, therefore, that it is essential to obtain definite information regarding, *inter alia*, the contamination of foodstuffs by containers and cooking utensils. The general question of absorption of metals by animal tissues demands accurate and reliable methods for the determination of small amounts of metals in organic materials.

We claim no more in the present paper than to have standardised a method for the determination of aluminium, and, in view of the difficulties later described with regard to the colour changes, we consider that our application of the Lovibond tintometer to the determination has rendered it sensitive and of a high degree of accuracy.

It is obvious that, for the determination of aluminium in food, two separate problems are involved:—(i) The development of a suitable process for the quantitative determination of the aluminium-content of a solution; (ii) The preparation, in as simple a manner as possible, of a solution containing the aluminium free from any substance which would interfere with the determination.

I. DETERMINATION OF THE ALUMINIUM-CONTENT OF A SOLUTION.—Of the various reagents which have been proposed for the detection of small amounts of aluminium, sodium alizarin sulphonate[1] and aurin tricarboxylic acid[2] have received most attention for the quantitative determination. We have investigated both these methods, and have preferred to use aurin tricarboxylic acid, since the colour-change from pale orange to intense red is more easily appreciated and more accurately matched in the Lovibond tintometer than the change from orange-yellow to orange-red, which occurs in the alizarin "S" method.

Aurin tricarboxylic acid was first proposed for the detection of aluminium by Hammett and Sottery,[2] and the details of their original test are as follows:

"To a solution containing the aluminium in 5 c.c. of *N* hydrochloric acid are added 5 c.c. of 3 *N* ammonium acetate and 5 c.c. of a 0·1 per cent. solution of the ammonium salt of aurin tricarboxylic acid. After the formation of the lake the solution is made alkaline with ammonium hydroxide containing ammonium carbonate. A bright red coloration or precipitate indicates the presence of aluminium."

This reaction has been applied to the quantitative determination of aluminium in organic materials by several workers. Thus, Myers, Mull and Morrison[3] used Nessler tubes, matching the unknown solution against colours prepared from standard aluminium solutions; they claim that the error ought not to exceed 10 per cent. Winter and Bird[4] give results obtained by using the method of Winter, Thrun and Bird,[5] and claim for them an accuracy within 5 per cent.; they used the Duboscq colorimeter. Beal (and others),[6] and G. J. Cox (and others)[7] used a similar method, but employed a permanent colour standard in place of prepared aluminium standards.

During the last six years we have had an opportunity of perfecting and standardising the technique now to be described, for, from a detailed study of the effect of various factors upon the stability, intensity and quantitative colour character of the aluminium lake produced by aurin tricarboxylic acid, it became clear to us that the procedure must be definitely controlled in order to obtain assured sensitivity and quantitative results. From a study of these factors we have accordingly developed a method which, followed strictly, gives the desired accuracy.

MODIFICATIONS AND STANDARDISATIONS OF THE PROCESSES

(*a*) *Stability of the Lake.*—We have found the addition of glycerol, as used by Atack,[1] in the alizarin "S" method, to be satisfactory for this purpose.

(*b*) *Colour Standards.*—For very small amounts of aluminium the colour obtained is orange, and as larger amounts are taken the amount of red colour increases and the yellow colour decreases until the colour is pure red. For still larger amounts the colour is bright bluish-red, the red, blue and brightness increasing as the amount of aluminium is increased. The importance of these colour changes has not been sufficiently realised, for it is apparent that a colorimeter of the Duboscq type cannot satisfactorily be used for the colour measurement unless the amounts of aluminium in the solutions to be compared are practically identical; the same objection applies to the use of a permanent colour standard. The use of Nessler tubes is a cumbersome process, involving the preparation of a range of standards for every determination.

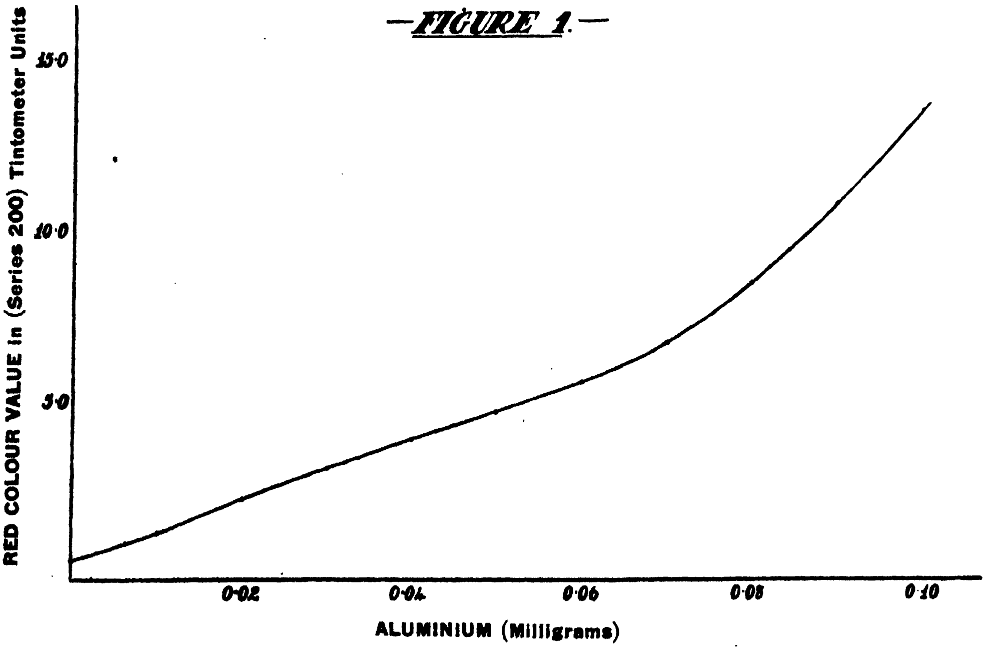
We have found that these difficulties are overcome by the use of the Lovibond tintometer. The method which we have adopted is to measure the tintometer colour values for solutions containing known amounts of aluminium, and to plot the red units on a graph which can then be used for determining the unknown aluminium content of other solutions. The direct comparison of one solution with another is thus avoided.

As will be seen from Table I, and from the graph in Figure 1, the red colour value (Series No. 200) is directly proportional to the amount of aluminium up to 0·06 mgrm. The yellow colour is obviously of no value as a factor for the determination.

TABLE I

Mgrms. of aluminium	Colour values of the solution in tintometer units		
	Red (No. 200)	Yellow (No. 510)	Blue (No. 1180)
nil	0·55	0·80	—
0·01	1·35	0·70	—
0·02	2·35	0·55	—
0·03	3·20	0·40	—
0·04	4·10	0·30	—
0·05	4·90	0·25	—
0·06	5·80	0·15	—
0·07	6·95	0·10	—
0·08	8·70	—	—
0·09	11·00	—	0·10
0·10	13·70	—	0·40

The red colour values for known amounts of aluminium are plotted in the graph in Fig. No. 1. The aluminium-content of a solution can, therefore, be calculated from a simple formula, *viz.* $(R-0{\cdot}55) \times 11{\cdot}5 \times 10^{-6}$ grms., where R is the red colour value of the solution in Lovibond units (Series No. 200), provided that R does not exceed 6 units.


—FIGURE 1.—

(*c*) *Preparation of Standard Aluminium Solutions.*—A series of standard aluminium solutions was prepared, using potassium alum, ammonium alum, and metallic aluminium, but it was found impossible to obtain concordant colour values for the different solutions. The difficulty was overcome by adding a small amount of hydrochloric acid to the standard solutions, and, when this was done, concordant results were obtained.

A somewhat similar fact is recorded by Pope,[8] who, in a recent paper, suggests that the loss of aluminium may be due to adsorption on the surface of the glass apparatus.

(*d*) *Standardisation of Conditions of Lake Formation.*—It is necessary to adopt a standard technique with regard to temperature and time, as well as the amounts of the reagents, since the final colour value of the solution is dependent on these factors, as well as on the amount of aluminium present. These points have been investigated by Yoe and Hill,[9] and by Winter, Thrun and Bird.[5] It has been shown that the lake formation is slow at ordinary temperatures, but that at about 100° C. it is rapid and complete. The colour fades after the addition of the ammonia and ammonium carbonate reagent, and the quantity added affects the actual colour-value of the solution, and also the rate of fading.

We have investigated the effect of these factors, and have found that uniformity of results can definitely be assured by heating the solution during lake-formation in a boiling water-bath for five minutes, and by subsequently cooling the solution in ice-cold water before the addition of the ammonium-hydroxide-carbonate solution. The colour is then measured in the Lovibond tintometer exactly five minutes after neutralisation with the ammonium-hydroxide-carbonate solution.

Winter, Thrun and Bird[5] claim that the fading of the final solution can be obviated by adjusting its *p*H to 7·1 to 7·3 with ammonium carbonate. Such a solution contains an excess neither of ammonium carbonate nor of ammonium hydroxide, and, in our opinion, this procedure is undesirable, since it makes no provision for the presence of small amounts of other metals, *e.g.* calcium, which might interfere.

RECOMMENDED PROCEDURE FOR THE DETERMINATION OF ALUMINIUM.—The procedure adopted for preparing the colour graph from the standard aluminium solutions or for determining the unknown aluminium-content of a solution to be analysed is as follows:

(*a*) *Reagents.*—*Standard Aluminium Solutions.*—1·757 grms. A.R. potassium alum, $Al_2(SO_4)_3.K_2SO_4.24H_2O$, is dissolved in water containing 25 c.c. of 5 *N* hydrochloric acid, and made up to 1,000 c.c. (1 c.c. = 0·0001 grm. aluminium). This solution is diluted 5 times to give a standard solution of which 1 c.c. = 0·02 mgrm. aluminium.

Hydrochloric Acid.—5 *N*.

Ammonium Acetate.—5 *N*. A solution containing 386 grms. of A.R. salt per litre.

Aurin Tricarboxylic Acid Reagent.—Two grms. of aurin tricarboxylic acid are dissolved in water containing a slight excess of ammonia. The solution is boiled to expel the excess ammonia, and is then made up to 1 litre with distilled water.

Glycerol Solution.—A solution containing equal volumes of water and glycerol. This is more convenient to use than pure glycerol.

Ammonium Hydroxide-Carbonate Solution.—Equal volumes of 10 *N* ammonium hydroxide solution and of 2 *N* ammonium carbonate solution are mixed. This solution should be kept in a well-stoppered bottle, and examined occasionally to ensure that it has not deteriorated through evaporation.

(*b*) *Analytical Procedure.*—The following details must be strictly followed:—Five c.c. of a neutral solution containing the aluminium are placed in a 100-c.c. conical flask; exactly 2 c.c. of 5 *N* hydrochloric acid, 5 c.c. of 5 *N* ammonium acetate, 20 c.c. of 50 per cent. glycerol, and finally, exactly 5 c.c. of aurin tricarboxylic acid reagent are added. The contents of the flask are well mixed, and the flask is immersed in boiling water for 5 minutes, and then cooled in a mixture of ice and water for at least 5 minutes. The contents of the flask are washed into a 50-c.c. graduated flask containing exactly 3 c.c. of the ammonia and ammonium carbonate solution, mixing the solutions at the time. After making up to the mark with water and mixing thoroughly, the colour of the solution is measured in the ½-inch cell in the Lovibond tintometer, exactly 5 minutes after the neutralisation with ammonia and ammonium carbonate solution.* Red slides of Series No. 200 are used.

II. PREPARATION OF THE SOLUTION FOR THE DETERMINATION OF ALUMINIUM FROM FOOD MATERIALS.—We have found that a satisfactory procedure by which all the aluminium in the sample is obtained in solution ready for determination as in (I), is as follows:—Ten grms. of the material are destroyed in a silica flask with nitric and sulphuric acids until a colourless residue is obtained. After cooling, this is diluted with 50 c.c. of water, care being taken to ensure complete solution of the aluminium sulphate (this precaution is necessary, if relatively large amounts, *e.g.* 100 parts of aluminium per million, are present). A slight excess of ammonia is then added, and the solution is boiled until the vapours no longer smell of ammonia. This operation is the most important stage in the determination, and is the only point at which a serious error may be made. The excess of ammonia must be removed, otherwise an appreciable loss of aluminium will occur. On the other hand, if the boiling is unduly prolonged, the solution becomes definitely acid, and the precipitated aluminium is re-dissolved. When the operation is correctly carried out, the solution is neutral to methyl orange. After boiling off the ammonia, the solution is filtered through a 9 cm. No. 41 Whatman filter, and washed with 10 c.c. of cold water. The filtrate should be tested with methyl orange.

The precipitate is dissolved from the filter paper with 15 c.c. of hot dilute hydrochloric acid (5 c.c. 5 *N* acid + 10 c.c. water), which is poured slowly, drop by drop, around the upper part of the filter paper, and the latter is then similarly washed with 10 c.c. of hot water. The acid and the washings are collected in the silica flask, and 10 c.c. of 5 *N* sodium hydroxide solution are then added. After boiling and cooling, the solution is filtered through a 9 cm. No. 54 Whatman paper, and the filtrate is collected in a 50-c.c. graduated flask. The silica flask and the filter paper are washed with cold water (15–20 c.c.) and, after cooling, the contents of the flask are made up to the 50 c.c. mark with water.

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* It will be noticed that the quantities used by us are somewhat different from those suggested by Hammett and Sottery. However, the essential feature of the test is the same, namely, the formation of the aluminium lake in an acetic acid and ammonium acetate buffer solution. The hydrogen-ion concentration of the above solution, and also that of the solution which would be obtained by adhering to the instructions of Hammett and Sottery, were measured. In both cases the *p*H was found to be 4·8.

An aliquot portion of this solution is taken for the aluminium determination and placed in a 100 c.c. conical flask. For an aluminium content between 5 and 50 parts per million of foodstuff, 5 c.c. is a suitable aliquot portion. (If a smaller aliquot part is taken, the volume must be made up to 5 c.c. with water.) Sufficient 5 *N* hydrochloric acid is added to neutralise the caustic soda present (*i.e.* one-tenth of the aliquot volume), and then 2 c.c. in excess. The colour value of the solution is then determined by the standard method already described.

Using the red colour value thus obtained, the amount of aluminium in the aliquot volume can be read from the graph, and the aluminium content of the food can be calculated, after correcting for the aluminium present in the reagents.

The necessity for removing the excess of ammonia was not at first appreciated; in fact a slight excess was purposely allowed to remain, and faintly ammoniacal wash water was used. The erratic results which were obtained are illustrated in the following table.

Table II

	Aluminium added Parts per million	Aluminium found Parts per million
Jam	24	22
	50	46
	100	73
Milk	15	2
	18	10
	25	6
	30	11
	30	21

In the case of the third determination on milk, the filtrate from the ammonia precipitation was boiled to expel the small amount of ammonia which remained, and was again filtered. The amount of aluminium recovered was equivalent to 19·5 parts per million, which made a total of 25·5 parts per million.

The effect of excessive boiling, beyond the point at which the excess of ammonia is expelled, is illustrated by the following determinations. The sample used was fruit pulp.

Aluminium added Parts per million	Aluminium found Parts per million
27	19
33	20·5

Our experience offers an explanation of the statements in the literature that it is not possible completely to precipitate small amounts of aluminium by a simple ammonia precipitation, *e.g.* Myers, Mull and Morrison.[3] It seems probable that aluminium hydroxide is slightly soluble in ammoniacal solutions, and this is in accord with the work of Hatfield and others,[10] who have shown that the minimum solubility zone of aluminium hydroxide is over the range *p*H 5·7 to 7·3 for ordinary bicarbonate drinking waters.

TYPICAL RESULTS OBTAINED BY THIS METHOD.—The results given in Table III have been obtained by the above method, known amounts of aluminium having been added to 10 grms. of food. A control determination was carried out on 10 grms. of the food *plus* reagents.

TABLE III

Material	Aluminium added Parts per million	Aluminium found Parts per million
Fruit pulp	30	30
Milk	50	51
	100	100
Jam	50	50
	100	100
Tomato purée	2	3
	10	10·5
	20	21

The possible interference with the accuracy of the method by other metals was investigated.

Various metallic salts, etc., together with known amounts of aluminium solution were added to samples of food, and the aluminium determined according to the procedure described. Results which are given in Table IV indicate that these added substances have not in any way interfered with the accuracy of the results for the amount of aluminium.

The procedure which has been outlined is that which we consider most convenient for ordinary use. If, instead of 20 c.c. of 50 per cent. glycerol, 10 c.c. of pure glycerol be used in the colour formation, then an aliquot part of 15 c.c. may be taken, and the method is capable of detecting and roughly estimating 2 or 3 parts per million in 10 grms. of food.

If the method is further modified so that the total filtrate from the sodium hydroxide precipitation is taken for the colorimetric determination, it seems probable that very small amounts could be detected and estimated, especially if more than 10 grms. of food be taken.

We have made some preliminary determinations by such a modified method, and we have been able to detect the presence of 0·2 part per million of aluminium in 20 grms. of food. This problem, however, needs further investigation, and we hope that it will form the subject of a subsequent communication.

THE ALUMINIUM-CONTENT OF FOOD COOKED IN ALUMINIUM VESSELS.—We have carried out a few experiments in order to give some indication of the amounts of aluminium which are liable to be present in foodstuffs which have been cooked in an aluminium saucepan. No attempt was made to carry out accurate corrosion tests, and ordinary culinary practice was followed.

TABLE IV

Foodstuff	Salts added equivalent to Parts per million	Aluminium added Parts per million	Aluminium found Parts per million
Fruit pulp ..	100 of copper	45	43
		10	12
	100 „ lead	40	41·5
		10	11·5
	100 „ tin	60	61
		59	57·5
		16	16
	200 „ tin	130	130·5
Jam	100 „ iron	33	34·5*
		3	2*
Fruit pulp ..	1000 „ iron	66	64
		20	19
Milk	50 „ zinc	98	96*
		19·5	18·5*
		1	1*
Fruit pulp ..	100 „ zinc	38	38·5
		14	15·5
	100 „ manganese	60	60·5
		12	13
Soup	100 „ nickel	77	78*
		17	16·5*
		7	7·5*
Fruit pulp ..	1 per cent. of P_2O_5	35	34·5
	1000 p.p.m. of calcium 1 per cent. of P_2O_5	50	53
		10	11
	1000 p.p.m. of manganese	10	9·5
	1000 p.p.m. of manganese 1 per cent. of P_2O_5	50	47·5
Tomato purée ..	Boric acid (200 p.p.m.)	21	21·5*
		3	3*
		1	1*

* It is of interest to note that in the case of the determinations marked with an asterisk the workers concerned had no idea of the amounts of aluminium present, or of the other added metals.

Tap Water.—London tap water was boiled for about half-a-minute, and then allowed to remain in the saucepan overnight.

	Aluminium-content
Before boiling	0·3 parts per million.
After boiling	2 „ „
After standing overnight	3·5 „ „

Milk.—An experiment similar to that with tap water was carried out, using fresh milk.

	Aluminium-content
Before boiling	0·4 parts per million.
After boiling	0·6 ,, ,,
After standing overnight	2·5 ,, ,,

Apples.—After peeling and coring, the apples were cooked for half-an-hour, with a little sugar and water.

	Aluminium-content
Before cooking	2 parts per million.
After cooking	14 ,, ,,

Tomato Soup.—The soup was prepared from peeled tomatoes and soup stock, and was cooked for half-an-hour.

	Aluminium-content
Before cooking	1 part per million.
After cooking	10 parts ,, ,,

Potatoes.—The potatoes were peeled and washed, and cooked in water containing 0·5 per cent. of salt for half-an-hour.

	Aluminium-content
Before cooking	2 parts per million.
After cooking	6 ,, ,,

Cabbage.—After washing, the cabbage was cooked for half-an-hour in water containing 0·02 per cent. of sodium bicarbonate and 0·25 per cent. of salt.

	Aluminium-content
Before cooking	8·5 parts per million.
After cooking	9·5 ,, ,,

NOTES ON THE DETERMINATION OF ALUMINIUM IN FOOD BY A SPECTROGRAPHIC METHOD

INTRODUCTION.—In addition to the colorimetric method described above, it was considered that the specific and positive evidence offered by the spectrographic method was of importance when dealing with small amounts of aluminium.

The work of previous investigators on the determination of aluminium in biological material was reviewed from the original work of Hartley[11] up to the present time. Faced with the special problem of the determination of aluminium in very diverse products with no foreknowledge of the amount of aluminium which might be present or of other mineral constituents, we have attempted to evolve from this published work and our own experience a suitable method.

EXPERIMENTAL PROCEDURE.—The method of wet destruction with sulphuric and nitric acids was employed, using 5 to 10 grms. of the material, as ashing may lead to losses of metals present in small quantities. The aluminium is precipitated from the resulting sulphuric acid solution (after dilution) with ammonia in the presence of ammonium acetate, filtered on No. 41 Whatman paper, dissolved in 5 N hydrochloric acid, and concentrated to 1 c.c. A portion of this is then evaporated in a trough cut in the electrode, and the residue is submitted to spark excitation. Copper electrodes were used and cleaned between exposures by soaking in 5 *N* hydrochloric acid, which was found to remove all traces of previous residues. The usual precautions were taken in the photographic procedure to ensure uniformity.

A blank was taken on the full amount of the reagents, the same procedure being followed as with a determination. The amount of aluminium found in the blank was $0{\cdot}4 \times 10^{-5}$ grm. A series of standards of various amounts of aluminium was prepared by passing them through exactly the same process of destruction, precipitation and concentration on the electrodes.

The determination was concluded by comparing the intensities of the experimental plates with the standards. Judgment by the eye alone was used, aided by a spacing of the spectra so that by super-imposing the plates any experimental spectrum could be brought between any two standards.

It was attempted in devising the technique either to minimise as far as possible the range of variations, or to conduct the analysis in such a way as to make the same variation occur in both the sample and standard spectra. It is still evident, however, that the greatest source of variation is in the variable nature of the spark, and this constitutes the source of the greatest inaccuracy.

Typical results are as follows:

Substance	Salts added Equivalent to parts per million of aluminium	Total aluminium determined Parts per million	Net aluminium determined Parts per million	Other metals, etc., Parts per million
Milk ..	0·0	0·3	Blank	
	0·2	0·2	—	
	0·9	1·2	0·9	
	1·3	0·9	0·6	
	0·0	0·5	Blank	
	0·7	1·1	0·6	
	1·1	1·75	1·25	
	1·5	2·0	1·5	
				Zinc
	19·6	13·0	13·0	50
	98·0	85·0	85·0	,,
	0·0	0·0	Blank	,,
	0·98	1·0	1·0	,,
				Boric acid
Purée ..	21·0	25·0	24·0	50
	0·0	1·0	Blank	,,
	1·0	Nil	—	,,
	3·0	3·5	2·5	,,
				Iron
Jam ..	3·0	1·5	1·5	100
	32·0	21·0	21·0	,,
				Nickel
Soup ..	0·0	2·5	Blank	100
	15·0	10·0	7·5	,,
	16·0	8·0	5·5	,,
	26·0	15·0	12·5	,,

The above table shows the results from a series of samples which had been prepared by the addition of aluminium and other salts by an independent worker in the laboratories.

Conclusion.—A method of concentrating the aluminium-content of a biological material on to an electrode has been devised so that no possible loss occurs. The spectrum is then excited by a condensed spark discharge modified to remove air lines, as far as possible, and a quartz spectrograph is employed to photograph the spectrum. The plate is developed under standard conditions, and then compared with sets of standards on plates prepared under precisely similar conditions.

The results show that aluminium is detectable down to 1×10^{-6} grm. or 0·1 part per million on a 10 grm. sample, and the intensities of the lines at 3944 and 3961·5A can be used to judge the amount present up to 2×10^{-5} grm.

The accuracy of the determinations does not compare favourably with that of the chemical method described above, but is sufficient for the purpose, namely, to confirm specifically that the contamination is due to aluminium, and that the amount found is of the right order.

The authors desire to thank Messrs. J. Lyons & Co., Ltd., in whose laboratory this work was carried out, for permission to publish; Miss M. Wilcox, B.Sc., Mr. A. N. Ainsworth, B.Sc., A.I.C., for assistance in the practical work; and Mr. E. B. Hughes, M.Sc., F.I.C., for helpful criticism.

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The Physiological Action of Aluminium*

By J. H. BURN, M.A., M.D.

(*Director of the Pharmacological Laboratory, Pharmaceutical Society of Great Britain*)

(*Read at the Meeting, June* 1, 1932)

Interest in the physiological action of aluminium and of aluminium compounds has been aroused, not only because of the use of aluminium for cooking vessels, but also because of the use of alum in baking powder. Little work has been done in this country, but much has been done in Germany and in the United States. The first work of importance was that of Siem, who published a dissertation in

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* The following account is an abbreviation of a review of the published information respecting the toxicity of aluminium and its compounds which I have written at the request of the British Non-ferrous Metals Research Association.

1886, giving an account of work done under Prof. Hans Horst Meyer in Marburg. Siem fed cats on sodium aluminium tartrate, giving daily doses corresponding with 0·1 grm. of alumina for four weeks. He observed an initial diarrhoea, but otherwise no effect of any kind. This dose given to an animal with a body weight of 2·5 kilos. corresponds with a dose of 2·5 grms. or 37 grains of alumina a day for a man weighing ten stone.

When injections were made under the skin, Siem found that the lethal dose for rabbits, cats and dogs ranged from 0·25 to 0·3 grm. per kilo.; no matter how large a dose was injected, death did not occur until after seven days. Siem's work, therefore, although undertaken nearly fifty years ago, established from the first what has, in the main, been confirmed by all subsequent workers, namely, that the daily consumption of relatively large amounts of aluminium in the food has no ill effects, though when aluminium compounds are injected under the skin they will cause death, provided the amount given is large enough.

To those who may think that, if a substance is toxic when injected, it must also be toxic when taken by mouth, the effects of magnesium compounds may be pointed out; magnesium and aluminium are related elements. The compounds of magnesium are harmless by mouth; we give magnesia to children as the most harmless of all laxatives, and many of them take it daily for years. Yet, introduced under the skin, magnesium compounds are toxic; a dose of crystalline magnesium sulphate from 1·0–2·0 grms. per kilo. (corresponding with about 0·1–0·2 grm. of magnesium per kilo.) produces immediate narcosis, and death after a short interval, in mice and in rabbits.

The toxic action of magnesium when injected is due to its narcotic action on the nervous system; death follows because of paralysis of the respiratory centre. To what is the toxic action of aluminium due? This has been studied by Siebert and Wells. These workers carried out a lengthy investigation in which they used rabbits, and in which they determined the effect of aluminium compounds after intravenous injection. They found that when 0·04 grm., or about two-thirds of a grain, of alum was injected every day into the ear vein of a rabbit (weighing about 2·5 kilos.), after two to three weeks the rabbit became anaemic. The percentage of haemoglobin, always decreased, and the number of red corpuscles finally declined in all the rabbits except one. The same decrease in the percentage of haemoglobin was observed in rabbits which received daily injections of 0·01 grm. of aluminium chloride. When these rabbits were killed and examined, the only pathological changes which the authors could attribute with certainty to the injections were in the spleen, where they found pigmentation, thrombosis, necrosis and fibrosis; the spleen changes were severe. There were also changes in the kidneys which were "presumably, truly an aluminium effect"; these were extensive vacuolation and granular degeneration of renal epithelium.

The physiological action of aluminium compounds, as indicated by the work quoted, is an action on the blood system, whereby the subject is rendered anaemic; this effect, however, is only observed when the aluminium compounds are injected, and not when they are given by mouth; by mouth they are without effect in ordinary amounts. It will be convenient to take this statement and consider how far it requires modification in the light of some of the different investigations which have been made.

EFFECT OF ALUMINIUM ON GROWTH AND REPRODUCTION.—Perhaps the most sensitive test of the harmfulness of any constituent of the diet is the effect of the constituent upon the growth of young animals. If a harmful substance is added to the diet of growing animals, it is common to observe that even when the animal is not obviously out of health, its growth-rate declines. In 1928, McCollum, Rask and Becker described the effect of adding aluminium chloride, and also alum baking powder, to the diet of young growing rats, so that the diet contained about 0·07 per cent. of metallic aluminium. It was observed that the growth-rate, reproduction and general health of the groups of rats receiving the aluminium were exactly the same as those of the control animals.

In the same year a similar piece of work was published by Myers and Mull (1928), also upon the effect of adding aluminium to the diet of young rats. Rats fed on a uniform diet were given 0·002 grm. of aluminium per rat for at least one hundred days, and during the course of the work four generations of animals were raised and the fifth was weaned. Growth in both the control and aluminium-fed groups was above Donaldson's normal for males and for females. There was a slightly more rapid initial growth of the aluminium-fed stock. This work is important, because the effect of aluminium was so thoroughly examined in successive generations of animals; if a harmful action had been exerted, it could not have escaped detection. The examination of the effect on growth was a quantitative examination in which composite growth curves for the different groups of animals were compared.

These two series of experiments by McCollum and his collaborators and by Myers and Mull furnish very important evidence, sufficient, I think, to convince all workers on nutrition that aluminium in the diet in small amounts is entirely harmless. The evidence these experiments provide, that reproduction is not affected, is of value because of the opposite conclusion reached by a group of French workers, Schaeffer, Fontès, Le Breton, Oberling and Thivolle. Schaeffer and his colleagues published a paper in 1928 in which they described the damage produced in the stomach and small intestine of mice by feeding them with aluminium compounds; this was severe. In dogs, however, the feeding with aluminium salts had no such effect, though the authors described areas of congestion in the large intestine. There were, however, no control observations on animals which had received no aluminium, and areas of inflammation in the large intestine of dogs, particularly of dogs abroad, may be due to many causes. Schaeffer and his colleagues were most impressed by the effect of aluminium-feeding on reproduction in mice, and thought that in these experiments they had the best evidence of the danger of aluminium in the diet. One experiment was as follows:—They took four groups each with ten pairs of mice; the first group was fed on bread with yeast, and in four months had 328 offspring; the second group was fed on the same diet, but had a larger percentage of a salt mixture and produced 310 offspring; a third group was fed on bread made with alum-phosphate baking powder, so that the diet contained 4·4 per cent. of aluminium: this group had only 192 offspring;

the fourth group had the same diet as the third, but only 1·3 per cent. of aluminium: it produced 244 individuals. The authors say "these results are so outstanding as to need no comment. They can be explained by an elective specific action of the aluminium ion on the ovary."

The deduction that the aluminium ion has a specific action on the ovary is unwarranted by the evidence, and reveals a very uncritical attitude on the part of these workers. No details of the experiments are given, and had the work indicated the harmlessness of aluminium rather than the opposite, the work would have been disregarded. It has, however, been quoted by those who think that aluminium is harmful. Even if, for the sake of argument, the work is accepted as trustworthy, it merely shows that when so large an amount of aluminium salts is added to the diet as to raise the content of aluminium to 1·3 per cent., the reproduction is reduced from about 300 to 250. This is scarcely noteworthy. Raising the aluminium percentage to 4·4 reduced reproduction from 300 to 200. At the worst, the only conclusion is that relatively enormous amounts of aluminium salts in the diet do not do more than restrict reproduction, and, as shown by the more dependable and fully documented experiments of McCollum and of Myers, smaller amounts have no effect whatever.

THE ABSORPTION OF ALUMINIUM FROM THE ALIMENTARY CANAL.—Much work has been done on the absorption of aluminium salts from the stomach and intestines into the blood stream, the animals employed being either rats or dogs. The best papers are those of Myers and Morrison (1928) and of Underhill and Peterman (1929). The actual results do not appear to differ greatly, but Underhill and Peterman conclude from their experiments that aluminium is promptly absorbed in small quantities following a single administration of food to which it has been added. The figures in support of this conclusion are given in Table I, taken from their paper.

TABLE I

ALUMINIUM AS MGRMS. PER 100 GRMS. OF WET TISSUE

Procedure	No. of dogs	Liver	Bile	Kidney	Brain	Heart	Spleen	Thyroid
1 week starving ..	12	0·94	1·9	0·84	1·25	0·19	1·84	7·25
1 week meat and bread	12	0·66	1·86	1·12	1·45	0·18	2·01	5·5
Single feeding ..	15	0·6	2·5	0·76	1·64	0·26	2·16	5·3
1 week feeding ..	6	0·84	2·27	0·50	1·63	0·5	1·85	6·1
1 week control ..	2	0·44	2·02	0·75	1·31	0·147	2·45	10·4
1 month feeding ..	6	0·73	1·75	0·65	1·20	0·29	2·12	5·2
1 month control ..	2	0·67	1·40	0·65	1·15	0·18	1·82	4·0
3 months feeding ..	6	0·83	1·95	0·54	1·19	0·19	2·41	6·1
3 months control ..	2	0·74	1·44	0·58	1·28	0·07	2·11	3·8

The figures show that aluminium is present in the tissues of starving dogs, as well as in those of dogs fed on meat and bread containing no aluminium. After a single feeding with food containing aluminium, there was a slight rise in the aluminium-content of the bile, the brain, the heart and the spleen; the rise in all these tissues is so slight, however, that it is surprising to find the authors drawing the conclusion already stated; moreover, after feeding aluminium for a week, the figures, except for the heart, are less than after a single feeding, so that it is even more puzzling that the authors should say "aluminium continues to be absorbed when aluminium-rich diets are fed for various periods of time."

The experiments of Myers and Morrison (1928) on the absorption from the alimentary tract were performed on dogs which received 0·23 and 1·55 grm. of aluminium daily for three months. These were compared with normal control dogs. There was almost no difference in the aluminium-content of the spleen, kidney and heart, but in the liver the aluminium-fed dogs had an average of 0·27 mgrm. of aluminium per 100 grms. of tissue, against an average of 0·15 mgrm. of aluminium per 100 grms. of tissue in the control dogs. When 5 mgrms. of aluminium were injected daily into two dogs for two weeks, an increase in the aluminium-content of the tissues was still evident as long as thirty-four days after the administration was discontinued, indicating that when aluminium is present in the tissues it is only slowly excreted.

These results fully support the conclusion that only traces of aluminium compounds are absorbed from the intestines.

EXPERIMENTS ON MAN.—It is not often that a medical problem can be put to the final and conclusive test of experiment on the human subject, and in the few cases in which it can, the result of the experiment is generally accepted as closing discussion once and for all. The agitation against the use of alum baking powder in the United States during the years 1911–1914 led to a formal investigation by the Department of Agriculture. The President of Johns Hopkins University was chosen as Chairman of a board, to which some of the most prominent American workers on nutrition were appointed. The board instituted three independent sets of experiments which were carried out on university students in different universities. The numbers of men used were twelve, six and eight, respectively, and these were given daily amounts of alum for a period of about six months, the daily amounts varying from 0·23 grm. to 10·0 grms. The food was all carefully measured and weighed, the excretions of urine and faeces were collected and analysed, daily records of body weight, temperature, respiration and pulse were kept for each man, and notes were made of any unusual symptoms. The results of the experiments in the three different universities were the same, and the conclusion that aluminium compounds present in small quantities in the food are harmless, was drawn by all three investigators. They state that amounts of aluminium up to 75 mgrms. a day are quite harmless; amounts up to 200 mgrms. may provoke mild catharsis, that is some looseness of the bowels; amounts up to 1 grm. per day usually produce catharsis.

It is obvious that this report of the United States Department of Agriculture is of great significance. Twenty-six human beings were deliberately fed with aluminium compounds for a period of six months, and careful observations of their health were made during this time. It was shown that, without exception, the subjects were entirely unaffected, except that large doses of aluminium salts caused mild catharsis.

THE AMOUNT OF ALUMINIUM COMING FROM COOKING UTENSILS.—The amount of aluminium coming from cooking utensils has been determined by different observers, and the most complete data I have found are those given by Massatch

(1929). He determined the amount of aluminium in the ash of a series of dishes such as scrambled eggs and bacon, cabbage, meat stew, soup, cakes, stewed apples, and cocoa. From the weights of the ingredients taken it is possible to calculate how much aluminium an individual would consume per day if he ate all these dishes. The result is given in Table II.

TABLE II

	Al_2O_3 Mgrms.
From scrambled eggs and bacon	0·06
From cocoa	0·6
From cabbage cooked in vinegar ..	5·5
From goulash	0·25
From bouillon with beef	0·45
From cakes	0·3
From apple sauce	6·0
Total	13·16

The total amount of 13 mgrms. of alumina corresponds to approximately one-tenth of a grain of aluminium. The small quantities of aluminium which the report of the United States Department of Agriculture states have no effect whatever, are up to 1·16 grains daily, or more than ten times as much as Massatch's figures indicate will come from aluminium utensils. This evidence should be sufficient to dispel any doubt remaining after the results obtained in the rat experiments have been fully considered.

CLINICAL OBSERVATIONS.—It remains to deal with certain clinical observations which have recently been made by various medical men. A pamphlet has been printed by Dr. Cooper and distributed among the medical profession. Dr. Cooper's statements are that many patients suffering from indigestion and abdominal pains are relieved of their symptoms if they cease to use aluminium vessels for cooking their food. Recently there has been some correspondence in the *British Medical Journal* on this subject, and two other medical men have written supporting what Cooper has said, one of them stating that the idea of aluminium being harmful was introduced to him by Cooper. One reply, in the *British Medical Journal* of April 23rd, contains the following:—"The letter of Dr. Coram James in your issue of April 9th is explainable as an interesting example of faith-healing. Believing aluminium cooking utensils to be harmful, he convinces his patients that the financial loss entailed in scrapping their aluminium ware will be beneficial to their health, and it is."

It is a commonplace of medicine to-day that many new remedies produce wonderful effects at first, but that soon they lose their efficacy; doctors like to get hold of these new remedies quickly to use them "while they still work." The explanation is that the new remedies cure by a psychological effect which ceases when the remedies are no longer new.

I, myself, have no doubt whatever that all the relief of pain which attends the discontinuance of aluminium cooking vessels is due to psychological forces. My own conviction, however, and the similar conviction of others, will not shake the opinions of those who think with Dr. Cooper; nor are they moved by experiments on animals.

In conclusion, there is one experiment which I think might be organised to answer such a letter as that in the *British Medical Journal* of April 16th from Dr. Alexander Francis. Dr. Francis says that he himself and six of his patients have got relief from abdominal pain by discontinuing the use of aluminium vessels. It is remotely conceivable that this is not a psychological effect, and that some people may be "anaphylactic to aluminium," as Dr. Francis expresses it. Why not test the matter? Let a number of these patients who imagine themselves sensitive to aluminium stay for some days in a hotel or house where it is arranged that they shall be given alternately food cooked in aluminium vessels and food cooked in other ware, without the patients knowing when the aluminium ware is used and when the other. The experiment would have to be arranged with care, but, if this were done, a clear answer might be obtained whether the aluminium ware did or did not give rise to symptoms in these patients, when psychological effects were excluded.

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DISCUSSION

The PRESIDENT thought that the paper by Dr. Lampitt and Mr. Sylvester had fulfilled a long-felt want. It seemed somewhat unfortunate that the American investigators had published rather lengthy lists of determinations of small amounts of aluminium in foods without mentioning how the results were obtained. One felt, perhaps, that the information lost a considerable amount of value because of this fact. Aluminium was not an easy element to determine. It had a characteristic—it formed an insoluble precipitate in the presence of ammonia, but there were two colour reactions, the one already described, and one which, he believed, Dr. Monier-Williams was going to mention later. The author of the last paper had mentioned the presence of alum in baking powder. So far as the President was aware, in this country this substance had disappeared from baking powder many years ago. He had no knowledge of its re-appearance. So far as the action of alkalis and acids on modern aluminium was concerned, he had had little experience, but some 20 or 25 years ago he had made determinations on the aluminium taken up by dilute acids and alkalis, and had been surprised at the extraordinary amounts taken up both by them and by common salt. They had had put before them that evening figures with regard to the aluminium taken into solution by weak salts, but he wondered whether the observer had taken into account the aluminium which was so often held loosely on the surface of the vessel after use. Not only did aluminium go into solution, but a considerable quantity was often loosened and very easily dissolved in any subsequent operation. He queried whether the metal determined was the metal both in solution and in suspension; also whether notice had been taken of the aluminium attacked. A result obtained after the action of a substance on clean aluminium might differ greatly from the result obtained by the action of the same substance on aluminium previously used and attacked as suggested. Dr. Burn had given a very fair resumé of the physiological effects of aluminium. He supposed that it was essential that this subject should be discussed, because scares had occurred both in Switzerland and in America, and therefore somebody certainly should be called upon to express views so that not only medical men, but also they, as Public Analysts, should have some idea as to the importance of the presence of small quantities of aluminium in food.

Dr. A. G. C. GWYER said that it had been his experience that aluminium was an element which did present difficulties in determination, and that these difficulties were always much greater when the analyst was not daily analysing aluminium. A statement had, for example, been made quite recently that milk exercised a very considerable solvent action upon aluminium, and, as he had always regarded milk as being without action, he had put in hand a series of experiments with the view to testing the truth of the statement. As was well known, the most common foodstuffs contained calcium, and it was therefore to the separation of aluminium and calcium that attention was directed. Separation might be effected in one of two ways: either the calcium could be removed and the aluminium determined in the filtrate, or the aluminium could be directly precipitated under conditions which ensured that the whole of the calcium present remained in solution. A possible precipitant was hydroxyquinoline, but this had not been found satisfactory for determining small amounts of aluminium in the presence of large amounts of calcium, whereas, on the other hand, the phosphate method had been found to work well, provided certain precautions were taken. Here Dr. Gwyer described the method in detail, emphasising that the *p*H value must be adjusted to between 4·5 and 4·0 in order to effect a complete separation. A similar conclusion had been reached by Patten and Winter, except that they had placed the upper limit at 5·3, which was, in his (Dr. Gwyer's) opinion, too high. Having decided upon the best method to follow, Dr. Gwyer had next carried out tests in which fresh milk was boiled in both new pans taken from stock and in an old pan, which had been in continuous use for over 12 months. In this case 250 c.c. of fresh milk were brought to the boiling point, boiled for 2 minutes, evaporated to dryness, and ashed, the acidity being adjusted to between *p*H 4·0 and 4·5 by the addition of acetic acid and sodium acetate. The precipitate was finally weighed as aluminium phosphate. Under the conditions described, the weight so obtained was 0·0002 grm., a value which was identical with that of the blank, and the conclusion reached, therefore, was that the milk had not dissolved any aluminium. The extreme importance of keeping the *p*H below 4·5 was demonstrated by an experiment upon a solution which contained a known small quantity of aluminium in the presence of a relatively large amount of calcium, the *p*H being purposely adjusted to 4·9. In this case the precipitate which was weighed consisted mainly of calcium phosphate, although it contained all the small quantity of aluminium present. With such a high degree of acidity it might have been supposed that the precipitate would have consisted of aluminium phosphate, and had the amount been calculated on this assumption, the aluminium present would have been returned as 120 grains per gallon, whereas the fact was that the aluminium-content was well under one grain per gallon.

Professor C. K. **Tinkler** said that they knew that some quantities were taken up where aluminium cooking vessels were used, and they knew, thanks to Dr. Lampitt and Mr. Sylvester, that it was possible to determine with very great accuracy these quantities. He was very interested to see that the amount taken up by milk was so small. Miss Masters and he had found, some years ago, that there was a definite protective action by colloids. He was particularly interested in Dr. Burn's paper, because it was necessary that the views of physiologists should be obtained on such a question as whether there was danger in using aluminium cooking vessels, and analysts were often asked such questions. People had written to him asking whether there was any danger in this. He told them that he did not think that, so far, any case had been made out against the use of such vessels, but he thought it unwise to store acid foods in aluminium containers longer than was necessary. He had referred the matter to his physiological colleague, who said that his rats which fed from aluminium containers in which food was kept for some time appeared to take no harm and were very healthy, although they must take up large quantities of aluminium. Of course, of this argument it might be said, as had been said before, "All men are not rats and only a few are guinea-pigs."

Dr. E. B. **Verney** said that in a cursory glance through the literature of the subject, two papers had attracted his attention. One was by Schmidt and Hoagland, who were working, he believed, for the Referee Board of the U.S. Department of Agriculture. They had fed men on foods containing aluminium. In one series of men as much as 300 mgrms. of aluminium was given per day for 70 days in succession, and 99·9 per cent. of the aluminium given was recovered from the stools. The second series was fed with dosages up to 500 mgrms. a day for 118 days, and there was almost an equally good recovery rate. An amount of 500 mgrms. per day per man would correspond with 50 kilos. of tomatoes per day, according to Mr. Sylvester's figures. It seemed perfectly clear that aluminium given by the mouth was a non-toxic substance to man.

The other paper was by Bertrand and Serbescu, published in the *Bull. Soc. de Chimie biologique* last year. These authors investigated the toxicity of aluminium, comparing it with iron and nickel, by means of injections of the sulphates into guinea pigs, determining the length of time which the animals survived after a large dose. Those injected with equivalent doses of copper and nickel died within an hour; those which were injected with zinc died within three hours, and those which were injected with iron or aluminium sulphate survived eight hours. They concluded that when the sulphates of these metals were injected subcutaneously, aluminium was no more toxic than iron.

In conclusion, even if it were proved that cases of super-sensitivity to small amounts of aluminium actually did occur, he did not consider that this would be any reason at all for forbidding the use or manufacture of aluminium ware. One could not legislate for people with idiosyncrasies; if we did, the use of most drugs would be prohibited—a sufficiently appalling thought for the medical profession.

Sir **William Willcox** said that it was always difficult to prove a negative, and that was rather the difficulty in which they were placed that evening. He had looked up certain forensic books and works on toxicology, and had not found aluminium, even in the index. Under "potassium" he had found "alum," and there was one case recorded in which a baby had died after taking several teaspoonsful of alum. If it had had several teaspoonsful of sand possibly the same thing would have happened. There was really no toxicological evidence that aluminium was poisonous. Most of the speakers that evening had made it clear that if aluminium was taken by the mouth it was not absorbed to any appreciable extent. The proof that aluminium was not absorbed was that such very minute quantities got into the blood, even when large doses were taken. Dr. Burn had quoted a paper in which it was shown that 99 per cent. of aluminium was recovered in the stools, after it had been administered by the mouth, which was a further demonstration of this point. The question of injections under the skin was not really under consideration. Many harmless foods, such as milk or beefsteak, would probably kill if injected under the skin.

Referring to fashions in medicine, Sir William mentioned the use of the term "allergical." This really applied to organic substances, and one could practically rule out the question of idiopathic idiosyncrasy with regard to metals. He had been practising medicine for a long time, and had seen many thousands of cases of ordinary dyspepsia, but never one in which the symptoms had been caused by aluminium. He had studied carefully the records of the clinical cases cited in the pamphlet to which reference had been made, and several of them appeared to him to be obviously attributable to something else than aluminium. In one case the patient, who had a temperature frequently, probably had a chronic appendix. The symptoms subsided, as these conditions did subside (especially when associated with auto-suggestion), well for a few months. Was it likely that aluminium was as terribly toxic as the author of the pamphlet would have us believe? Aluminium was present everywhere, and people were bound to swallow a lot of it. It seemed inconceivable, therefore, that the slight amount from aluminium cooking vessels could have any toxic effect. It was difficult to keep pace with all the patent medicines, but four or five years ago there was one called "Alocol," which was the very latest for the treatment of dyspepsia, gastric ulcers, etc. It was aluminium hydroxide, and was given in doses of 1 grm. from three to six times a day. To-day the fashion was kaolin, which was aluminium silicate; it often contained more than the legal amount of arsenic, so that if aluminium was harmful, he was sure that kaolin must be.

At present the position, from all that could be learned from scientific experiment and chemistry, was that there was no ground for stating that aluminium, as derived from cooking utensils, was harmful, but let open minds be kept, for, as he had already said, it was very difficult to prove a negative. To the best of his knowledge, however, there was no evidence that aluminium was harmful.

Professor J. C. **Drummond** said that it was not easy to get so clear a view as Dr. Burn had presented because of the conflicting nature of the evidence in the literature. It was, of course, a matter of very great difficulty to reach a decision on the toxic action, if any, of such substances as aluminium salts. If tests on small animals, such as rats, failed to give definite results, it was always possible to investigate their action on man. The experiments made by the U.S. Dept. of Public Health were, however, open to criticism, mainly on the grounds that the doses administered were fantastically large when compared with those which might be consumed under normal conditions. Largely on the basis of such experiments, the use of borates as preservatives was condemned. Nevertheless, it was well-known that the workers in the boric acid districts of Italy showed normal health in spite of constant absorption of comparatively large amounts. It was not acclimatisation, for new workers from other districts did not suffer on being brought into the boric acid areas. Similarly, there was no evidence that workers in daily contact with aluminium salts experienced any harmful effect.

Dr. R. **Seligman** said that, speaking as one who must bear a great amount of responsibility for the use of aluminium in the preparation of foodstuffs in this country, he would like to say how much he appreciated the fact that this subject was being brought on to the platform of a scientific society. He would like to draw attention to the relation between the two papers. They had heard from Dr. Burn the "evidence in the case." They had heard that there was no evidence of the toxic effect of aluminium, but that was not quite enough for those intimately concerned in this matter. They felt that they must know more than that there was no evidence. Therefore it was only as a first step in the investigations which they planned that they asked the Non-Ferrous Metals Research Association to select some gentleman to review the existing evidence. That Dr. Burn had done, and the results he had given. But Sir William Willcox had pointed out that it was difficult, if not impossible, to prove a negative of that kind. It was precisely there that the value of such a paper as that of Dr. Lampitt and Mr. Sylvester came in. He might say that the Association's second step was to have been a research to establish some reliable method of estimating very small quantities of aluminium. Luckily, the Association had been saved that, and they now had one colorimetric and one spectroscopic method of determining these small amounts. Therefore, they had advanced two steps in a very short time.

The importance of Dr. Lampitt's work was here: It was a commonplace that aluminium was everywhere; it formed just on 15 per cent. of the weight of the globe, and it was said to be in waters and in foods, and since time immemorial cooking had been done in clay vessels. What they wanted to know was whether it was really present in the foods eaten every day, because, if it were so present, he could not see how the suggestion of the special susceptibility to aluminium poisoning of some people could possibly be true. Dr. Burn, in his paper, had referred to a statement of Dr. Francis in the *British Medical Journal*. Dr. Francis had said that he was so sensitive to the effects of aluminium that if he tasted food cooked in aluminium vessels (even if no method of analysis was able to show traces of the metal) he immediately diagnosed it by suffering severe abdominal pains. One must set against that such work as that of Mme. Lévy, at the Pasteur Institute, who examined 55 common vegetables for aluminium, and whose results compared closely with those of Dr. Lampitt and Mr. Sylvester. We now had the results obtained by a number of methods of analysis, all different, which all came to the same result—that practically in all these foods there were appreciable quantities of aluminium present. Dr. Gwyer had explained away a statement in the pamphlet, which had been referred to several times that evening, to the effect that milk cooked in an aluminium saucepan dissolved 140 grains of metal per gallon in a few minutes. That statement struck him as amazing; he did not know whether the meeting realised its implication. He calculated that it meant that 3 tons of dissolved aluminium were being supplied with the milk to Londoners every day.

On behalf of those working in this matter, he wished to say that they did not consider the book closed or the chapter ended as yet. They were most anxious to test by any means which came to their knowledge whether the metals used by them were toxic in any way. He could quite believe that modern statistical methods might reveal some physiological effect of aluminium, but it would not be open to any honest man, after that evening, to speak of aluminium as a strong irritant poison.

Dr. T. C. Hunt mentioned that he had had a few patients, who had been convinced that they were suffering from aluminium poisoning. There were three, in particular, all of whom had assured him that their symptoms had ceased from the moment they stopped taking food cooked in aluminium vessels. In his opinion, it was almost conclusive that such a sudden cessation of symptoms implied a psychological basis. Could it have been from absorption of aluminium, the symptoms must surely have ceased gradually and have died away as the metal was gradually excreted. One saw so often the effect, as had already been pointed out, of faith and suggestion, particularly in matters relating to digestion. One had not any sort of clinical condition that could be attributed to aluminium. He thought that a fuller investigation of the excretions of some of the patients who attributed their symptoms to aluminium was needed, and a set of test experiments, such as Dr. Burn had suggested, with and without aluminium in the food, would be very useful.

Dr. R. S. Hutton, speaking as Director of the British Non-Ferrous Metals Research Association, which asked Dr. Burn to investigate this matter, asked if he might be allowed to thank the Society for the opportunity of bringing this question before it. Dr. Drummond had pointed out that there was always a great risk in questions of this sort of some interested body taking a particular side and fostering some action for or against some particular material. His own Association was so conglomerate that all rival metals came within its purview. This matter was referred to the Association, and on behalf of them he went to the very highest authorities. As a first step, they were advised to get an impartial review of all the literature, and Dr. Burn was mentioned as being able to give a perfectly independent review of the matter. As far as he knew, Dr. Burn knew and cared very little about aluminium at the time. They were prepared and anxious, not only to make a review of the subject, but actually to put in hand any clinical or other research which might throw light on the subject. Their present opinion was that there was very little more to be done after this review, but they would be only too ready to consider any suggestions put before them for further research or study which would be useful.

Mr. H. W. Webb said that he might be able to contribute a few words on the analytical aspect of the subject. Two years ago he had published, in collaboration with Dr. Schoeller, a paper on the application of tannin to the precipitation of various earth-forming metals (Analyst, 1929, **54**, 711). They were able to prove that the bulky tannin precipitates were very suitable for the determination of small quantities of thoria, zirconia, titania, and alumina. A previous separation from iron by means of ammonium sulphide was readily carried out in ammoniacal tartrate solution, the filtrate from the ferrous sulphide being faintly acidified with acetic acid, boiled, and the aluminium precipitated with tannin in presence of ammonium acetate.

As regards the precipitation of alumina in presence of phosphoric acid, they had obtained some precipitates in which no phosphoric acid could be detected by molybdate, but others contained small amounts. Even if the final alumina precipitate had to be corrected for a small phosphoric acid content, he believed that the method would be very convenient for the determination of the minute amounts of alumina encountered in foodstuffs. A quantity of alumina of the order of 0·5 mgrm. could easily be handled without the use of special micro-apparatus.

Dr. G. **Monier-Williams** (in a written communication) said that, in his experience, the hydroxy-quinoline method of Berg was the most satisfactory for the determination of aluminium in foods. Iron and aluminium were precipitated together as phosphates from a solution of the sulphated ash, and the iron was subsequently separated as basic acetate. Aluminium was precipitated in the filtrate as the hydroxy-quinoline compound, which was filtered off and titrated with $N/10$ bromate-bromide solution. Five c.c. of this solution were equivalent to about one milligramme of aluminium.

The experimental work so far carried out in his laboratory indicated that most, if not all, of the aluminium reported to exist naturally in fruits and vegetables was due to dust and dirt on the surface. If the surface were thoroughly cleaned with soap and water before analysis, the amount of aluminium in the sample was reduced to vanishing point. Fruits and leaves with rough or sticky surfaces naturally retained dust, and therefore showed, on analysis, an appreciable amount of aluminium. Little or no evidence had so far been obtained that aluminium was a normal constituent of the ash of plants.

Dr. S. **Judd Lewis** referred to a paper which he had published on the determination of aluminium in blood and milk by the arc-method of quantitative spectrography (*Biochem. J.*, 1931, **25**, 2162; Analyst, 1932, 324). In a considerable number of experiments he found usually no aluminium in normal blood, but the blood of subjects fed with one scone containing 94 mgrms. of aluminium once a day for any number of days up to 14, showed a fairly constant aluminium-content of about 1 part per 1,000,000 of blood; but in one case it increased greatly. The earliest time at which aluminium was observed in the blood was 4·5 hours after administration, but it was much more evident after 24 to 48 hours. It showed quite early in the milk, both in humans and in cows and goats. Cows were drenched with a dose of aluminium immediately after one milking, and it was found in the milk of the next milking. This was rather important in connection with the absorption of aluminium.

Mr. F. R. **Stephens** observed that nothing had been said about the consumption of aluminium in the presence of a certain amount of organic acid. His own personal experience was that it had a very definite effect if taken in considerable quantity. All the cases mentioned had related to more or less neutral solutions, but in a strongly acid solution, such as tartaric or acetic acid, would aluminium not have some physiological action?

Major **Stanley Elliott** said that in the Army alum had been used for many years for clarifying water, without any injurious effect on the troops. Moreover, the cavalry had used an aluminium water-bottle, in which was placed sodium bisulphate, giving the water a *p*H value of 3, and making it sterile. This water contained about a grain of aluminium per gallon, the amount, of course, depending on the period of contact, and the statistics did not show that the British trooper suffered from anaemia or gastric troubles to any greater extent than the rest of the Army which used the enamelled iron bottle.

With regard to Dr. Cooper's pamphlet, he had been asked by the Director of Hygiene to check the chemical results. He found that the figures in most cases were wrong; in the experiment on soup it was stated that about 300 grains of aluminium per gallon were found—this would give a life of only about 20 stews of soup to a 3-ounce pan. Everyone was aware that aluminium pans had been in use for years in ordinary houses. He had found practically no difference in the action of foods on so-called "cast" and "spun" aluminium pans, the former being the thick material, the latter the thin metal. The method used was that of Hammett and Sottery, slightly modified in a different way from Dr. Lampitt's method, and he found that it gave excellent results, but, as iron gave a purple colour which interfered seriously with the matching of the colours in the test, it was very necessary to get rid of the iron. The results he obtained by heating foods in aluminium vessels were similar to those obtained by Dr. Lampitt and Mr. Sylvester. As the whole point of Dr. Cooper's objections to aluminium lay in the lesions in the intestine supposedly caused by its passage, he would like to know whether Dr. Burn had noticed any damage to the intestines of animals subjected to the action of aluminium in their food.

With regard to the tolerance of metals by people, the arsenic eaters of the Tyrol had acquired a high degree of tolerance to this substance, and other metals could be tolerated in comparatively large amounts; was it possible that a tolerance to aluminium could be acquired by human beings?

Miss H. **Masters** said that they had heard a great deal about cooking utensils. She would suggest that, from the practical point of view, the question might be raised as to what materials likely to be less harmful should be used as an alternative to aluminium. The choice of materials which could be used for cooking utensils was limited, and it was not a case of being able to select one which would yield nothing at all, but of trying to select the one which was least likely to yield injurious products. She welcomed the discussion that evening because it had shown that there was very little possibility of any harm being caused by the use of aluminium cooking utensils.

Mr. L. J. **Odling** enquired whether Mr. Sylvester had made any experiments with softened water, such as was so often used in households to-day for cooking purposes.

Dr. K. **Mackenzie** said that he had made one or two physiological experiments in connection with the absorption of aluminium into blood. He had started on the basis of work of Underhill, who had fed dogs with a certain amount of aluminium, and had found aluminium subsequently in the blood, but on attempting to repeat the experiment on rabbits no aluminium at all could be detected in most cases. He then injected aluminium into the blood, and subsequently examined the blood. He was rather surprised that it did not show any aluminium, seeing that aluminium sulphates or solutions rather acid in character were being used. It was found that at least 50 per cent. of the aluminium could be recovered from the liver of the animal. He then went on to use the neutral solutions (aluminium tartrate), and in that case, also, on injecting about 1 mgrm. in solution, most of the aluminium disappeared in a very short time—within about one hour—and again, about 50 per cent. was found in the liver. He could not get any higher recovery. Next he introduced aluminium into the intestine of the animal and examined the portal blood to see whether the aluminium was carried by that course. It seemed possible that if aluminium were inserted into the small intestine it might travel in the blood stream into the liver and possibly be deposited there. An animal was anaesthetised, and about 1 mgrm. of aluminium tartrate in 10 c.c. of physiological saline was introduced into the intestines. Samples of portal blood were taken at intervals of 30 minutes, 1 hour and 2 hours, and it was found that very little of this aluminium had travelled, and upon subsequent examination of the intestine at least 95 per cent. could be recovered. This still left, of course, a 5 per cent. margin, and there seemed little doubt that some aluminium was transported in this way, but its amount was very slight.

Mr. A. SCIVER asked if Dr. Burn had come across any information in the literature with regard to the effect of traces of aluminium on bacteria, because of the possible connection between physiological action and oligodynamic action. It had to be assumed that aluminium was normally present in foodstuffs, but he did just wonder whether the form in which it was present might not make a difference. He did not think it a fair assumption to make that, since aluminium was present and harmless in kaolin, it was necessarily harmless when present as an acid salt in, say, fruit juice.

Dr. H. J. STERN raised the question of the purity of the aluminium used. The purer the aluminium the less it would be dissolved. He thought it might be that some of the older work was done with aluminium of less purity than that used at present.

Mr. E. HINKS said that he trusted that nothing that had been said during the evening would be construed as offering justification for the intentional introduction of aluminium compounds into food, for instance, alum in bread. Alum baking powders had fallen into disuse in this country, and their re-introduction would have to be considered apart from the question of traces of aluminium derived from cooking utensils.

Mr. A. SAMSON said he was interested in the remarks of Dr. Stern in connection with the purity of aluminium cooking vessels as used for analytical tests. Speaking from a practical point of view, especially in the case of cooking meats containing 2 to 5 per cent. of salt, his experience had been that vessels purchased 5 or 6 years ago did not last long, but that those vessels purchased 2 or 3 years ago were standing up much better. The salt seemed to have a very marked effect on aluminium vessels. Perhaps Dr. Seligman could say whether vessels constructed to-day were made of aluminium of greater purity than was the case a few years ago.

Dr. SELIGMAN, referring to the question whether there was a direct comparison between the effect of various acids and these foodstuffs on aluminium, said that there was one very striking case. If lactic acid, equivalent to the amount in milk, were taken, the aluminium would dissolve very readily, but the addition of a little milk to the mixture would stop the attack altogether. That fully illustrated what the President suspected might be the case.

During the last 20 or 30 years there had been an enormous improvement in the quality of aluminium produced, especially in this country. But the point was this: he knew of no aluminium, however inferior, which could have given such results as Dr. Cooper had published.

Mr. SYLVESTER, replying, thanked the President and the audience for the very kind way in which they had received the paper. Referring to the corrosion of aluminium vessels which were not perfectly clean, he mentioned some recent work by Beal (and others) in the April issue of *Industrial and Engineering Chemistry* (ANALYST, 1932, 392). These workers had found a larger amount of aluminium in foodstuffs cooked in stained utensils, thus emphasising the necessity for keeping aluminium vessels scrupulously clean. One speaker had asked whether there would be larger amounts of aluminium present when acid fruits were cooked in aluminium, and Mr. Sylvester quoted figures given in the paper by Beal (and others). Cranberry sauce gave 8 parts per million, which, in the presence of sugar, was decreased to 3. Rhubarb gave 13 parts per million, and in the case of apricots, the aluminium-content increased from 25 to 73. He thought that the latter figure should be accepted with reserve.

The question of cooking in soft water, and the possibility of such water being more corrosive than ordinary tap water had been mentioned, but Mr. Sylvester stressed the fact that the few experiments which had been included in the paper, must not be considered as a scientific investigation of the corrosion of aluminium. They were carried out with the essential object of proving that the method of analysis described was applicable to such problems as corrosion or contamination, and they indicated also the amounts of aluminium likely to occur in foodstuffs as the result of ordinary culinary practice.

Dr. BURN, replying to the question about the action of aluminium on bacteria, said that some work had been done on the subject.

In explanation of the way he had presented the paper he did not pretend that what he said was an impartial survey of the situation. He had already written an impartial survey in the form of a more lengthy report, but it seemed to him that if he were to deal with the subject in twenty minutes the best thing was to put before them the strongest evidence in support of the conviction he had reached.

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A New Method for the Determination of Lead in Organic Material, with Special Reference to Dyestuffs

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(*Read at the Meeting, February* 3, 1932)

THE determination of lead in complex organic material, such as dyestuffs and biological specimens, has always been a troublesome analytical procedure. Gravimetric methods are not well suited to the accurate determination of traces of lead, and even when sufficient material is available to yield weighable quantities of precipitate, the process of separation becomes very complicated when silica or metals such as calcium, iron, or tin are present. It is, therefore, proposed to consider, in this paper, only those processes depending upon colorimetry.

Most of the colorimetric methods depend upon the final conversion of the lead into sulphide, the solution containing the lead being first rendered alkaline. It is obvious that when lead is detected under these conditions, iron and interfering metals must either be absent or, if present, the formation of their sulphides must be prevented. Removal of iron by precipitation as hydroxide is inapplicable, since lead will be adsorbed by the precipitate. In order to eliminate the influence of iron, F. L. Teed (ANALYST, 1892, **17**, 142) proposed the addition of potassium cyanide with the object of forming either ferrocyanides or ferricyanides. This method was elaborated by C. A. Hill (*Chem. and Drug.*, 1905, **77**, 388), who adapted it to the determination of lead in pharmacopoeial chemicals. The processes described are well suited to the purpose for which they were devised, but it is clearly indicated that the presence of iron in more than minute traces will interfere with the colorimetric determination. J. M. Wilkie (*J. Soc. Chem. Ind.*, 1909, **28**, 636) stated that potassium cyanide would eliminate the influence of ferrous iron, but that the ferric iron vitiated the test; he, therefore, recommended preliminary reduction by heating with sodium sulphite or sodium thiosulphate in slightly acid solution, followed by the addition of potassium cyanide and ammonia. In practice, this method frequently proves difficult to operate, and, in any case, it is not applicable in the presence of more than a few milligrams of iron. Furthermore, with many dyes, even when these are free from iron, the accurate determination of lead by direct methods is not practicable, since the residues remaining after wet oxidation are frequently yellow in colour, owing, probably, to the formation of nitro bodies resistant to further attack by the mixture of nitric and sulphuric acids.

Recently the problem of determining small amounts of lead in biological material has been dealt with by A. G. Francis, C. O. Harvey and J. L. Buchan (ANALYST, 1929, **54**, 725). Briefly, their process involves preliminary wet oxidation of the organic material; the addition of a small quantity of a copper salt; co-precipitation of the lead and added copper by means of hydrogen sulphide; conversion of the sulphides into sulphates, followed by solution in dilute nitric acid, and then separation of the lead from other metals yielding dark coloured sulphides by electrolysis, the lead being deposited as dioxide on the anode. The lead dioxide is dissolved in dilute nitric acid and alcohol, and the lead is precipitated as lead sulphate; this is dissolved in ammonium acetate solution, and the amount of lead present is determined colorimetrically as sulphide. The presence of appreciable amounts of iron will interfere with the electrolytic deposition of lead dioxide, and, in this event, it is necessary to make a preliminary separation of the lead by precipitation as sulphate. The whole process is stated to require about three days to complete, and is, therefore, unsuited for rapid routine work in connection with the examination of dyes and foodstuffs.

Other colorimetric methods for the determination of lead have not proved very satisfactory. The use of tetramethyldiaminodiphenylmethane, suggested by A. Trillat (*Ann. Chim. anal.*, 1903, **8**, 408), involves the electrolytic deposition of the lead as dioxide; in addition to this disadvantage, the reagent yields colours with manganese dioxide and many other oxidising agents.

A process due to L. T. Fairhall (*J. Biol. Chem.*, 1924, **60**, 485) for the determination of lead in urine comprises co-precipitation of the lead with calcium phosphate by rendering the sample alkaline with ammonia, dissolving the lead from the ignited precipitate with dilute nitric acid, conversion of the lead successively into sulphide, sulphate, sulphide and chromate; the chromate is then determined colorimetrically by the use of diphenylcarbazide. In this process the colour produced is due to chromium and not directly to lead. Francis, Harvey and Buchan (*loc. cit.*) criticise this procedure, and also express some doubt as to the efficacy of co-precipitation of lead with calcium phosphate. Again, the process is tedious, since one determination takes six days to complete.

For the diagnosis of plumbism, T. Cooksey and S. G. Walton (ANALYST, 1929, **54**, 97) determine traces of lead in the urine by electrolysing in acid solution, dissolving the lead from the cathode with nitric acid, and removing the latter by evaporation. The residue is then dissolved in hydrochloric acid, and the lead is determined nephelometrically as sulphite. This process, which requires 24 hours to complete, can only be used in those cases where it is known that all the lead is present in an ionisable form.

It occurred to us that diphenylthiocarbazone might prove useful in dealing with the problem under review. The constitution of this compound is represented by the formula $C_6H_5.N{=}N.CS.NH.NH.C_6H_5$, and its behaviour towards metals has recently been described by H. Fischer (*Z. angew. Chem.*, 1929, **42**, 1025, and *Mikrochem.*, 1930, **8**, 319), who used a solution in carbon tetrachloride containing a few milligrams of the reagent per 100 c.c. of solvent. This solution is deep green in colour and, when it is agitated with an aqueous alkaline liquid containing lead, the green colour changes to red, owing to the formation of a metallic compound, which is soluble in the organic layer but insoluble in water. Fischer describes the colours produced by several metals under these conditions, and states that the reaction with all metals, lead only excepted, is inhibited by the presence of alkali cyanide. In addition to this, the reagent does not appear to react with iron under any circumstances; it therefore seemed to promise a ready means for the specific removal of lead from the residues remaining after the wet oxidation of organic material. Diphenylthiocarbazone was first prepared by E. Fischer and E. Besthorn (*Annalen*, 1881, **212**, 316) from phenylhydrazine and carbon disulphide. Since it is now an article of commerce, and the pure substance is readily available, further description of its preparation is unnecessary.

DEVELOPMENT OF THE PROCESS.—As this work was undertaken with the object of determining traces of lead in dyestuffs, all the experiments have been conducted on that class of organic material. Since the determination of the lead involves the preliminary destruction of the organic matter by the well-known process of wet oxidation with sulphuric acid and nitric acid, it is obvious that the conditions will be identical for all dyes and all organic substances, subject to such limitations as may be imposed by the presence of various inorganic constituents, apart from the lead. At the outset attempts were made to match the actual red colour due to the presence of lead when the residues from the wet oxidation of lead-containing dyes were diluted with water, then rendered alkaline and mixed with a little potassium cyanide, and finally shaken with very dilute solutions of diphenylthiocarbazone in carbon tetrachloride. It soon proved, however, that this procedure was impracticable, since the gradations of colour produced by varying amounts of lead were too slight to allow of accurate measurement. It was evident that in order to determine the amount of lead extracted it would be necessary to convert the metal into some compound other than the salt of diphenylthiocarbazone. Experiments were, therefore, made, in which the organic solvent containing the lead complex was evaporated, and the dry residue which remained was destroyed by wet oxidation, using only about 0·5 c.c. of sulphuric acid. The resulting colourless acid liquid was then diluted with water, ammonium acetate, excess of ammonia and potassium cyanide were added, and the lead was determined colorimetrically as sulphide in the usual manner.

Working on these lines, promising results were soon obtained, but carbon tetrachloride was found to be unsuitable as a solvent for the reagent, owing to the sparing solubility of diphenylthiocarbazone. A mixed solvent, consisting of three parts by volume of carbon tetrachloride and two parts by volume of benzene, was tried and gave good results, but chloroform was found to be much superior. The reagent ultimately adopted consists of a 0·1 per cent. w/v solution of diphenylthiocarbazone in chloroform. This solution may be stored in stoppered bottles without undergoing deterioration for about a fortnight.

METHOD.—The process, as finally worked out, is as follows:—A suitable quantity of the dyestuff, or other organic material, is destroyed by wet oxidation by heating with sulphuric and nitric acids, and the residue is freed from nitric acid by diluting with water and evaporating until white fumes are evolved. After being cooled, the acid solution is diluted with water, 2 grms. of citric acid are dissolved in the liquid, which is then rendered alkaline with ammonia, and 1 c.c. of 10 per cent. solution of potassium cyanide is added. The cooled solution, which should conveniently amount to 100 to 150 c.c., is transferred to a separator and extracted three times by shaking vigorously with a 0·1 per cent. w/v solution of diphenylthiocarbazone in chloroform. Ten c.c. of the reagent solution should be used for the first extraction, and 5 c.c. each for the second and third. Should the third extraction be bright red in colour, it will be necessary to continue the extraction with more reagent until the red colour is no longer produced. Each extract is washed in turn with about 10 c.c. of water contained in another separator, and transferred to a flask, and the chloroform is evaporated. About 0·5 c.c. of sulphuric acid is added to the residue, and the organic matter is destroyed by heating and adding to the hot sulphuric acid solution a few drops of nitric acid. This residue, which will contain all the lead originally present in the material taken for the determination, is diluted with water, 2 grms. of ammonium acetate are added, and the liquid is rendered alkaline with ammonia. The lead is then determined by adding 1 c.c. of 10 per cent. potassium cyanide solution, then 0·1 c.c. of 10 per cent. sodium sulphide solution, and matching the colour in the ordinary way by means of the Dilute Solution of Lead PbT. of the British Pharmacopoeia (which contains 0·00001 grm. of lead per c.c.), using an auxiliary solution containing 2 grms. of ammonium acetate. If more than 0·1 mgrm. of lead is present, aliquot portions of the solution should be taken, more ammonium acetate being added as necessary.

When examining dyestuffs, it is recommended that the wet oxidation be conducted according to the methods detailed in the First Report of the Sub-Committee on the Determination of Arsenic, Lead and Other Poisonous Metals in Food Colouring Materials to the Standing Committee on the Uniformity of Analytical Methods (ANALYST, 1930, **55**, 102). This report is concerned with the determination of arsenic in colouring materials; hence, provided the relative quantities of the acids used are maintained, it should be admissible to employ a larger amount of the sample at the outset, and to divide the final acid liquid in two portions, one being used for the arsenic determination and the other for the determination of lead.

When a milligram or more of lead is present in the final sulphuric acid residue the lead sulphate will be clearly visible, particularly if all the nitric acid is removed by evaporating down a second time after diluting with water.

The citric acid used in this method serves the two-fold purpose of dissolving lead sulphate present in the sulphuric acid residue, and also of preventing iron from being precipitated when the liquid is rendered ammoniacal. Potassium cyanide is added to the aqueous liquid, prior to shaking with the reagent solution, in order to prevent other metals being extracted by the diphenylthiocarbazone. It is not used to prevent the extraction of iron, since that metal does not react with the reagent at all; it is, nevertheless, necessary to maintain the iron in solution by the addition of citric acid in order to prevent loss of lead by adsorption. When the amount of lead present is more than a fraction of a milligram the green reagent solution used in the first extraction will turn bright red, and additional portions of reagent will change similarly until all the lead is removed from the aqueous layer. In this way a rough indication of the amount of lead present in the sample is obtained at an early stage of the process. In the absence of lead a considerable proportion of the reagent dissolves in the alkaline aqueous layer, colouring that solution orange. While the reagent itself is soluble in alkaline aqueous media, and is thereby partly extracted from the chloroform solution, the lead compound is insoluble in the aqueous liquid, but readily soluble in chloroform.

TEST EXPERIMENTS.—To test the efficacy of this process, experiments were first made with a specimen of very pure indigo-carmine, practically free from iron. The lead in the sulphuric acid residue from the wet oxidation was determined directly by ordinary colorimetric methods and found to be 30 parts per million. Exactly the same result was obtained when another portion of the same dye was examined by the new process described.

Experiments were made with this same sample of dye to which known amounts of lead had been added, and the results obtained are shown in Table I.

TABLE I

Amount of dye used for the test Grms.	Lead solution added c.c.	Lead solution found c.c.
1	5·0	5·0
2	5·0	4·5
2	20·0	19·0
2	140·0	142·0
5	80·0	80·0
2	500·0	503·5

The quantities of lead in the tables are expressed in terms of the Dilute Solution of Lead PbT. of the British Pharmacopoeia. In quoting the quantity of lead recovered (column 3), the amount of lead originally present in the material, together with the "blank" due to the reagents, has been deducted.

THE INFLUENCE OF OTHER SUBSTANCES.—In studying the effect of other substances on the process, attention was mostly directed to metals, and particularly to iron. Early experiments had shown that the presence of even 1 per cent. of iron in a dye did not interfere with the detection and determination of the lead. A series of tests was now made, in which the proportion of iron in the dye was increased by mixing it with known quantities of ferrous ammonium sulphate, and adding definite volumes of standard lead nitrate solution; the mixture was then submitted to wet oxidation, and the lead was extracted and determined by the process described. In all these experiments a very pure dye was employed, and the lead-content was determined by a colour test applied directly to the residue remaining after wet oxidation. In this way the value of the "blank," due to the minute trace of lead present in the reagents and the dye itself, was determined independently of the new process. Some of the results of these trials are shown in Table II.

TABLE II

Material treated	Lead solution added c.c.	Lead solution found c.c.	Remarks
1 grm. of dye+0·21 grm. of ferrous ammonium sulphate (=3 per cent. Fe in dye).	10·0	9·5	
2 grms. dye+0·84 grm. of ferrous ammonium sulphate (= 6 per cent. Fe in dye).	7·0	7·6	
1 grm. of ferrous ammonium sulphate	6·0	5·7	
5 grms. of ferric sulphate [77 per cent. $Fe_2(SO_4)_3$].	10·0	10·0	Used 10 grms. of citric acid. No trace of iron in final matching solution.
5 grms. of ferrous sulphate cryst.	30·0	30·0	Oxidised the ferrous iron by boiling with HCl and $KClO_3$.
2 grms. of ferric sulphate + 1 grm. of ammonium nitrate.	8·0	5·2	Effect of nitrate.
5 grms. of ferric sulphate [77 per cent. $Fe_2(SO_4)_3$].	500·0	473·0	Used 10 grms. of citric acid.
5 grms. of ferric sulphate [77 per cent. $Fe_2(SO_4)_3$].	120·0	120·0	Used 10 grms. of citric acid.

Another point to which we have given particular consideration is the actual weight of impurity present in the material under examination, as distinguished from the percentage present in the dye. Working on these lines, we found that lead could be added to 5 grms. of ferric sulphate, and be fully recovered and determined colorimetrically. In no case did iron pass through into the final solution, although the added lead was regularly recovered within the limits of experimental error. It was at this stage of the investigation that the mixed solvent of carbon tetrachloride and benzene used to dissolve the diphenylthiocarbazone was abandoned in favour of chloroform, since it was found impossible completely to extract the lead from 5 grms. of iron salt until this modification was tried. On reference to Table II, it will be noticed that ferrous sulphate was oxidised by means of potassium chlorate and hydrochloric acid. When the oxidation was conducted with nitric acid in the presence of sulphuric acid there was difficulty in removing the excess of nitric acid, owing to the tendency towards violent bumping, with consequent loss of material. This residual nitrate tends to interfere with the complete extraction of lead, particularly in the presence of a large proportion of iron. The effect of adding ammonium nitrate to ferric sulphate is shown in the table. Thus, it was proved that iron, even when present in quantity, does not interfere with the determination of lead by this method.

Bismuth.—The process is inapplicable in the presence of bismuth. This metal, if present, will pass through and yield a coloured sulphide. Bismuth is not a likely impurity in dyestuffs, but if this process is applied to toxicological investigations or to metallurgical analysis, special care will, of course, be needed.

Zinc.—Having regard to the fact that some dyestuffs consist of zinc double salts, it was considered important to study the influence of this metal. Reference to Table III shows that the addition of 1·8 grm. of zinc sulphate to a dye does not interfere in any way with the determination of lead. It was observed, however, that when the lead was extracted in the presence of zinc the reagent became bright red in colour, even after all lead had been removed, owing to the reaction with the zinc. Thus, it should be borne in mind that in the presence of much zinc a bright red colour produced by the reagent is not necessarily an indication of a large content of lead.

Aluminium.—Aluminium may cause trouble by reason of the formation of an insoluble anhydrous sulphate during the wet oxidation of the organic material. Reference to Table III will show that where complete solution of the aluminium salt was not effected prior to the extraction process, much of the added lead remained behind as a result of being adsorbed upon the solid suspension. When this experiment was repeated, and the diluted acid liquid was heated for some time with a little potassium sulphate, the soluble alum was re-formed, and complete recovery of the added lead obtained, in the subsequent extraction. Further, to prove this point, an experiment was made with alum itself, and the added lead was satisfactorily recovered.

Copper.—The presence of copper is quite immaterial, provided care be taken to add sufficient potassium cyanide to form the non-ionised complex. While investigating the influence of this metal it was thought that it might be possible to avoid the initial wet oxidation of dyestuffs, and use instead a dry process employing copper nitrate. In order to test this, 2 grms. of the pure specimen of indigo-carmine, previously mentioned as being used for checking purposes, and containing 30 parts per million of lead, were mixed in a porcelain crucible with 3 grms. of anhydrous sodium carbonate and 10 grms. of copper nitrate, $Cu(NO_3)_2.3H_2O$. By the application of gentle heat, using a small Bunsen flame, all organic matter was readily destroyed, and the copper nitrate was decomposed to oxide at a temperature so low that loss of lead by volatilisation could not occur. The cooled residue was dissolved by heating with 20 c.c. of concentrated hydrochloric acid, and the clear liquid, after dilution with water, was treated with citric acid and excess of ammonia, the blue colour of the solution being discharged by the addition of 14 grms. of potassium cyanide. The extraction and colorimetric determination of the lead were then effected by the method already described. The final solution used in the colorimetric determination of the lead yielded a perfect match. A blank experiment on the reagents was made, 2 grms. of lead-free citric acid being used in place of the dye. By this method the lead-content of the dye was found to be 40 parts per million. This procedure is only suggested as a possible alternative to wet oxidation, should the latter be inconvenient to apply. Where the lead-content of the material under examination is low, oxidation with copper nitrate is not recommended, since the value of the "blank" tests is necessarily large; but for organic material containing appreciable quantities of lead the method may well be useful. Experiments have shown that at least 5 mgrms. of lead can be easily and completely extracted from the residue of a copper nitrate fusion.

Tin.—Traces of tin will not influence the working of the process, but if appreciable quantities are present, certain modifications must be introduced. The insoluble "meta-stannic acid" resulting from the wet oxidation should be dissolved. This can generally be accomplished if the sulphuric acid residue is carefully diluted with about 50 c.c. of a 5 per cent. aqueous solution of tartaric acid, and then rendered alkaline with sodium hydroxide solution, care being taken that the temperature does not rise appreciably until the mixture is alkaline. It should then be heated until a clear liquid is obtained. After the addition of a little potassium cyanide the lead is extracted in the ordinary manner. Traces of tin may still pass through with the lead; this trouble can be overcome by evaporating the chloroform and submitting the residue to wet oxidation in the usual way and, after removal of all nitric acid, treating the sulphuric acid residue a second time in the manner just described, and then re-extracting the lead. This somewhat tedious procedure may not always be necessary, and is only indicated in the presence of considerable quantities of tin. Some results obtained in the presence of tin are quoted in Table III.

Calcium phosphate does not interfere. Any material originating from calcium phosphate, or other salts of calcium, contained in the acid residue after wet oxidation should be dissolved by diluting with water and treating with excess ammonium citrate solution. The ordinary process may then be applied.

Silica.—In order to test the effect of appreciable amounts of silica, samples of dye were mixed with dried sodium silicate and, after the addition of known volumes of standard lead solution, they were submitted to wet oxidation. The resulting residues were extracted in the usual way, the insoluble silica being ignored. Full recovery of lead was obtained, thus demonstrating that it is unnecessary to apply any special treatment for the removal of silica.

Nickel.—The process may be applied in the presence of nickel, but it is necessary to guard against incomplete extraction of the lead. Satisfactory results were obtained in the presence of 1 grm. of nickel sulphate when six portions of reagent were used to remove the lead from the aqueous solution.

Cobalt also tends to retard the removal of lead, notwithstanding the presence of an excess of potassium cyanide. This difficulty was surmounted by heating the solution containing cobalt with sufficient ammonium chloride, ammonia and hydrogen peroxide to produce a cobaltammine. After excess hydrogen peroxide had been boiled off, a little hydrazine sulphate was dissolved in the solution to reduce any lead peroxide which might have been formed. Citric acid and 1 c.c. of 10 per cent. solution of potassium cyanide were then added, and the usual procedure was followed.

Silver, mercury, manganese, and *chromium* do not interfere with the extraction and determination of lead. An exhaustive examination of the influence of these four metals has not been made, but the experiments quoted in Table III would suggest that none of them is likely to cause much difficulty.

From a consideration of the work here described it would appear that diphenylthiocarbazone might be applied to metallurgical analysis. Our process has been designed for the purpose of dealing with traces of lead, but it may be

TABLE III

Material treated	Lead solution added c.c.	Lead solution found c.c.	Remarks
1 grm. dye + 0·022 grm. of zinc sulphate (= 0·5 per cent. Zn in dye).	5·0	5·0	
2 grms. dye + 0·88 grm. of zinc sulphate (= 10 per cent. Zn in dye).	20·0	20·0	
2 grms. dye + 1·8 grm. of zinc sulphate (= 20 per cent. Zn in dye).	95·0	98·0	Used 1 grm. of potassium cyanide.
2 grms. dye + 0·175 grm. of potassium alum (= 0·5 per cent. Al in dye).	8·0	8·0	Aqueous liquid before extraction of lead was clear.
2 grms. dye + 3·5 grms. of potassium alum (= 10 per cent. Al in dye).	5·0	2·2	Aqueous liquid before extraction of lead was hazy. Lead adsorbed.
2 grms. dye + 3·5 grms. of potassium alum (= 10 per cent. Al in dye).	10·0	10·0	Aqueous liquid cleared by heating after addition of potassium sulphate.
5 grms. potassium alum	10·0	9·8	
1 grm. dye + 0·4 grm. of copper sulphate (= 10 per cent. Cu in dye).	8·0	8·2	Used 2 grms. of potassium cyanide.
1 grm. dye + 0·0095 grm. stannous chloride (= 0·5 per cent. Sn in dye).	6·0	5·8	Used tartaric acid and sodium hydroxide.
5 grms. dye + 0·0475 grm. of stannous chloride (= 0·5 per cent. Sn in dye).	25·0	26·4	Lead extracted once only. Sulphide colours did not match well.
2 grms. dye + 0·38 grm. of stannous chloride (= 10 per cent. Sn in dye).	4·0	3·6	Extracted the lead a second time. Perfect colour match obtained.
2 grms. dye + 1 grm. of calcium phosphate.	10·0	9·5	Added excess ammonium citrate solution to residue after wet oxidation.
2 grms. dye + 2 grms. of calcium phosphate.	6·0	6·5	Added excess ammonium citrate solution to residue after wet oxidation.
2 grms. dye + 0·5 grm. of dried sodium silicate.	10·0	10·0	Aqueous liquid before extraction of lead contd. insoluble silica in suspension.
2 grms. dye + 2·0 grms. of dried sodium silicate.	15·0	15·0	Aqueous liquid before extraction of lead contd. insoluble silica in suspension.
2 grms. dye + 1·0 grm. of nickel sulphate (= 10·4 per cent. Ni in dye).	10·0	10·2	Used 2 grms. of potassium cyanide and six portions of reagent solution.
2 grms. dye + 1·0 grm. cobalt nitrate (= 10 per cent. Co in dye).	10·0	10·0	Heated with $NH_4Cl + NH_4OH + H_2O_2$. Reduced PbO_2 with $N_2H_4.H_2SO_4$.
2 grms. dye + 0·5 grm. of silver nitrate (= 15·9 per cent. Ag in dye).	5·0	5·0	Used 2 grms. potassium cyanide.
2 grms. dye + 0·5 grm. of mercuric chloride (= 18·5 per cent. Hg in dye).	5·0	5·2	Used 2 grms. potassium cyanide.
2 grms. dye + 2 grms. of manganous sulphate + 1 grm. potassium permanganate.	10·0	10·0	Added HCl to residue after wet oxidation.
2 grms. dye + 0·5 grm. of potassium dichromate.	8·0	7·8	

possible by making suitable modifications, such as increasing the strength of the reagent solution, to extract much larger quantities of lead from its association with other metals.

SUMMARY.—A new method has been described for the determination of lead present in organic material. The whole process can easily be completed in two hours, and is, therefore, eminently suited to the routine examination of dyestuffs required for medicinal and food-colouring purposes.

A special feature of the process is its applicability in the presence of large quantities of iron. It has been shown that traces of lead present in salts of iron can be detected and accurately determined.

Bismuth interferes with the test, and special procedures are necessary when appreciable amounts of tin, aluminium, nickel or cobalt are present.

Silica and calcium phosphate do not present any difficulties, and large quantities of copper, zinc, silver, mercury, manganese, and chromium may be present without vitiating the determination of the lead.

In conclusion, we wish to record our thanks to Mr. T. T. Cocking, F.I.C., for his valuable advice and interest during the course of this work, and to the Directors of The British Drug Houses, Ltd., for permission to publish the results of the investigation.

Investigations on Milk Standards under the Burma Food and Drugs Act, 1928

BY EDWIN H. BUNCE, F.I.C.

(*Read at the Meeting, February* 3, 1932)

A LARGE number of samples of both cow's and buffalo's milk, from herds and from individual animals, were examined throughout a period of eleven months.

The herds were systematically studied at regular intervals, so that seasonal variations could be observed and a fair average obtained.

In the case of the individual animals, however, the samples were taken at random from various localities, the object being to study the quality of milk of the poorest types of animals. The animals were chosen on the advice of an officer from the laboratory, specially deputed for the purpose, and he also witnessed the milkings.

The yield of morning milk was greater than that of evening milk drawn from the same animals, but the milk was of poorer quality in respect of fat. These results, of course, are associated with the interval between the milkings. In general, the period from evening to morning was 13 to 14 hours, and that from morning to evening 10 to 11 hours. Exceptionally, in the case of the buffalo herds during the months of August to November, the period from evening to morning was 15 to 16 hours, and that from morning to evening 8 to 9 hours. This was, perhaps, unfortunate, but unavoidable, and consideration of the results obtained demonstrates still more forcibly the effect of milking at unequal intervals.

Cow's Milk.—The number of mixed herd samples examined was 200. The fat and total solids were determined directly by the usual analytical methods, and in a few instances these figures disagreed with Richmond's formula.

The average results of all samples were:

TABLE I

	No. of samples	Fat Per Cent.	Solids-not-fat Per Cent.	Total solids Per Cent.	Ash Per Cent.	Sp.gr.	Acidity*
Morning milk	100	3·63	9·30	12·93	0·76	1·0333	1·5
Evening milk	100	5·19	9·30	14·49	0·74	1·0325	1·5
Average	All samples	4·41	9·30	13·71	0·75	1·0329	1·5

* Number of c.c. of $N/10$ sodium hydroxide solution per 10 c.c. of milk.

The average figure for solids-not-fat was remarkably constant, and no appreciable variation was observed in the average figure for fat throughout the period of the investigation. These facts are brought out clearly in Table II. No herd samples gave a percentage of solids-not-fat below 8·5 per cent., and only one gave a fat figure below 3·0 per cent.

The number of samples examined from individual cows was 90. As already mentioned, these samples were taken from different localities, and were in no way connected with each other. In some cases the animals could hardly be said to be properly kept and fed. Such milk is sometimes exposed for sale, however, and that was the main reason for their inclusion in the investigation.

In two cases the solids-not-fat were below 8·5 per cent., and seventeen samples gave a fat figure below 3·0 per cent.

Standards.—No legal standards for cow's milk are at present in operation in Burma, but the laboratory has adopted a minimum of 3·0 per cent. for fat, and 8·5 per cent. for solids-not-fat. The latter figure is a lenient one, and although a number of samples gave slightly less than 3·0 per cent. of fat, only one of these was from the mixed herd. Since the greater part of milk for sale is the product of more than one animal, the standard of 3·0 per cent. for fat cannot be said to be stringent.

TABLE II

AVERAGE PERCENTAGE OF FAT AND SOLIDS-NOT-FAT IN MIXED SAMPLES FROM HERDS

	Period	Fat Per Cent.	Solids-not-fat Per Cent.	Total solids Per Cent.
Morning milk	April–July	3·74	9·28	13·02
Evening milk		5·09	9·30	14·39
Average		4·42	9·29	13·71
Morning milk	August–November	3·49	9·21	12·70
Evening milk		5·29	9·21	14·50
Average		4·39	9·21	13·60
Morning milk	December–March	3·71	9·40	13·11
Evening milk		5·14	9·40	14·54
Average		4·42	9·40	13·82
All samples	April–March	4·41	9·30	13·71

TABLE III

SHOWING SAMPLES GROUPED ACCORDING TO THEIR FAT AND SOLIDS-NOT-FAT CONTENT

Total No. of samples	Below 3·0 per cent. fat		3·0–3·5 per per cent. fat		Below 8·5 per cent. solids-not-fat		8·5–9·0 per cent. solids-not-fat	
	No. of samples	Per Cent.	No. of samples	Per Cent.	No. of samples	Per Cent.	No. of samples	Per Cent.
200 (from herds)	1	0·5	38	19·0	—	—	20	10·0
90 (from individuals)	17	18·9	10	11·1	2	2·2	31	34·4

BUFFALO'S MILK.—The number of mixed herd samples (from *Bubalus buffalus*) examined was 200. The analytical methods employed were precisely the same as those adopted for cow's milk.

The average results of all samples were:

TABLE IV

	No. of samples	Fat Per Cent.	Solids-not-fat Per Cent.	Total solids Per Cent.	Ash Per Cent.	Sp.gr.	Acidity*
Morning milk	100	6·78	10·16	16·94	0·79	1·0336	1·2
Evening milk	100	7·98	9·92	17·90	0·77	1·0330	1·0
Average	All samples	7·38	10·04	17·42	0·78	1·0333	1·1

* Number of c.c. of $N/10$ sodium hydroxide solution per 10 c.c. of milk.

Again it will be seen from Table V, below, that the average figure for solids-not-fat is remarkably constant. The drop in fat-content for the morning milk, with a corresponding rise for the evening milk, during the period August to November, is accounted for by the change in the times of milking, as given above. However, it will be noticed that the results obtained by averaging the fat-content of both morning and evening milk during this period, in no way deviate from the other average figures similarly obtained. No herd samples gave a percentage of solids-not-fat below 9·0, and only three samples gave a fat figure below 5·0 per cent.

The number of samples examined from individual buffaloes was 76. These samples were taken at random, and the same statements apply as in the case of individual cow samples in this respect.

In no case was the figure obtained for solids-not-fat below 9·0 per cent., although there were several only just above that figure. The fat-content of two samples was below 5·0 per cent.

Standards.—As in the case of cow's milk, standards for buffalo's milk have not yet been legally defined in Burma. A minimum of 5·0 per cent. for fat, and of 9·0 per cent. for solids-not-fat, is applied in the laboratory in passing judgment on samples. No final opinion on the purity or otherwise of a sample of milk received for analysis is given, however, without recourse to cryoscopic examination.

Similar remarks apply to samples of cow's milk submitted for analysis.

TABLE V

AVERAGE PERCENTAGE OF FAT AND SOLIDS-NOT-FAT IN MIXED SAMPLES FROM HERDS

	Period	Fat Per Cent.	Solids-not-fat Per Cent.	Total solids Per Cent.
Morning milk	April to July	.7·16	9·96	17·12
Evening milk		7·90	10·00	17·90
Average		7·53	9·98	17·51
Morning milk	August to November	5·94	10·29	16·23
Evening milk		8·58	9·99	18·57
Average		7·26	10·14	17·40
Morning milk	December to March	7·06	10·11	17·17
Evening milk		7·64	9·88	17·52
Average		7·35	10·00	17·35
All samples	April to March	7·38	10·04	17·42

TABLE VI

SHOWING SAMPLES GROUPED ACCORDING TO THEIR FAT AND SOLIDS-NOT-FAT CONTENT

	Below 5·0 per cent. of fat		5·0–5·5 per cent. of fat		Below 9·0 per cent. of solids-not-fat		9·0–9·5 per cent. of solids-not-fat	
Total No. of samples	No. of samples	Per Cent.	No. of samples	Per Cent.	No. of samples	Per Cent.	No. of samples	Per Cent.
200 (from herds)	3	1·5	9	4·5	—	—	1	0·5
76 (from individuals)	2	2·6	4	5·3	—	—	18	23·7

APPLICATION OF CRYOSCOPY

Rigid control of the milk supply is a much more complicated problem in India and Burma than in England, mainly owing to the fact that the milk of at least two animals of different species is involved.

The milk from cows and buffaloes is often mixed indiscriminately, with or without the addition of water or other substances, but more often the buffalo milk is watered so as to mimic the composition of cow's milk, and then sold as such. Buffalo's milk being much richer in every respect, the fraud has been perpetrated with great success, water being added in almost every proportion.

It was obvious from this that the ordinary standards alone were hopelessly inadequate, and that some other means would have to be evolved to check adulteration effectively. The cryoscopic method suggested itself as a possible solution of the problem, since it was noticed that the soluble salts of the two milks approached more closely to each other than any of the other constituents normally present.

An apparatus modelled on the principle of the Beckmann cryoscope was employed, the accessories being readily available. The more elaborate Hortvet type would have been preferred, but, owing to the difficulty experienced in procuring that apparatus in reasonable time, its adoption would have meant the curtailment of cryoscopic measurements during the first six months of the investigation.

Application of correction factors was avoided by a carefully standardised procedure, so that the results obtained were strictly comparable. As a preliminary experiment the accuracy of the method was demonstrated with a series of known mixtures of authentic samples with water.*

All the samples described above were tested. They were perfectly fresh in all cases, and showed no tendency to souring.

A summary of the results is given in Tables VII and VIII.

TABLE VII

COW

Total No. of samples	Range	Average
200 (from herds)	—0·550° C. to —0·580° C.	—0·573° C.
90 (from individuals)	—0·550° C. to —0·580° C.	—0·567° C.

TABLE VIII

BUFFALO

Total No. of samples	Range	Average
200 (from herds)	—0·560° C. to —0·590° C.	—0·579° C.
76 (from individuals)	—0·560° C. to —0·590° C.	—0·578° C.

In view of these results a freezing-point figure outside the ranges shown must be considered unsatisfactory, and for the purpose of deducing the percentage of added water —0·550° C. has been adopted as the freezing-point of cow's milk, and —0·560° C. as that of buffalo's milk.

The relatively small difference of 0·01° C. between the two values is of greatest importance. Such difference corresponds with less than 2 per cent. of added water. Any attempt, therefore, to water buffalo's milk so that the lower standards for cow's milk are complied with is almost impossible, and cannot fail to escape detection if a cryoscopic examination is carried out.

My thanks are due to my Chief Assistant, Mr. G. C. Moitra, B.Sc., who carried out a considerable amount of the experimental work, and also to the other members of my staff who materially assisted in the investigation.

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* The apparatus was filled with a mixture of crushed ice and salt to serve as a freezing medium. A sufficient quantity of the sample (previously cooled) to submerge completely the thermometer bulb was placed in the freezing-tube, and the thermometer, together with the stirrer, was inserted. The test tube was then lowered into the larger tube of the apparatus.

Uniform stirring at the rate of about once per second was then applied, and the temperature of the cooling bath was adjusted, so that a supercooling of the sample between 1·0° and 1·5° C. was readily obtained. The mercury column rose rapidly to its highest point, when the reading was taken after tapping the upper end of the thermometer two or three times. By this method ten to twelve determinations were easily carried out within an hour.

The zero point of the thermometer was ascertained by observing the freezing-point of recently boiled and cooled distilled water under the same conditions. This point was checked whenever a new series of determinations was made.

Care was taken that the curvature of the bottom of the freezing-tube was not too pronounced; otherwise efficient stirring was difficult.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

MILK OF THE AMERICAN BUFFALO

Two samples of buffalo (*Bison americanus*) milk, submitted by the Veterinary Research Station, Lethbridge, Alberta, have recently been analysed in these laboratories. The first sample, received February 1st, and to which 0·1 per cent. of formalin had been added as a preservative, had slightly curdled in transit. The second sample, received March 19th, and to which 0·25 per cent. of formalin had been added, was perfectly sweet and fluid on arrival at Ottawa. Analysis gave the following results:

	No. 1	No. 2
Specific gravity	—	1042·0
Total solids (direct determination) ..	12·97 per cent.	13·67 per cent.
Fat	1·83 ,,	1·69 ,,
Casein	3·66	4·24
Albumin	0·64	0·54
Lactose	3·73(?)	5·74
Ash	0·86	0·96

Owing to the partial coagulation of the milk, some of the results obtained with the Sample No. 1 are doubtful, so that the analysis cannot be accepted as absolutely representing the composition of the fresh milk.

The following pertinent information respecting the buffalo producing the milk has been kindly furnished by Mr. L. M. Heath, the officer in charge of the Station.

"Born May, 1924. Received at the Veterinary Research Station from Wainright Buffalo Park, December 4th, 1924.

"Kept in corrals from date of receipt until October, 1926; then turned into pasture with other domestic cattle.

"Bred to domestic polled bull (no particular breed), July–August, 1928. Calved June, 1929 (first hybrid offspring).

"Bred to domestic polled bull, January 8th, 1931. Calved November 1st, 1931 (second hybrid offspring).

"The milk samples you analysed were collected as follows:—The first (curdled) sample, January 26th, 1932; the second, March 15th, 1932.

"It will be seen, therefore, that the samples were collected on the eighty-seventh and one hundred and thirty-sixth days, respectively, after the second gestation period.

"No great difficulty was experienced in collecting the samples of milk. Restraint was, of course, necessary, and was procured by means of a 'squeeze.' The 'squeeze' in question is a narrow alleyway, one side of which is adjustable, so that pressure can be brought to bear on an animal in the alleyway to prevent undue movement, the animal being in the natural standing position. The samples were obtained by hand-milking.

"There is no great mammary development in the buffalo as compared with that of cattle, and its teats are rather short. Owing to the small size of the udder the milk secretion is of necessity limited in quantity, and it was estimated that not much in excess of a litre was secreted overnight (about 15 hours) at the time the second sample was collected for your analysis."

Frank T. Shutt.
(*Dominion Chemist.*)

Department of Agriculture,
Ottawa, Canada.

MECHANICAL WOOD PULP IN PAPER

The determination of the mechanical wood content of papers by the phloroglucinol method, which forms the subject of a recent communication by Dr. Dunnicliff and Mr. Suri (ANALYST, 1932, 354), has of late become of greater importance, in consequence of the Indian Import Tariff on papers, "in which the mechanical wood pulp amounts to not less than 65 per cent. of the fibre content," and it has been stated that raising the percentage to 70 per cent. is being considered.

It has been all too apparent, however, that the use of the phloroglucinol method, unstandardised to Indian conditions, is unreliable. The method used by Cross and Bevan, which has been widely used, was not standardised, and had certainly not been devised with any regard to its present-day importance. Messrs. Dunnicliff and Suri have now standardised the process systematically.

The other available method most widely used is the "fibre count" microscope method of examining a series of mounts and estimating, by eye, the relative proportions of the fibrous ingredients present; the average accuracy for a series is no better than *plus* or *minus* 5 per cent. for ordinary fibres, and probably no better than *plus* or *minus* 10 per cent. for mechanical wood, which is always present in lumps and clumps. This method was formerly used in India in assessing tariff duty payable and, not unnaturally, its use gave rise to difference of opinion and dissatisfaction. In dealing with borderline and disputed cases, the method of Cross and Bevan was used to confirm or reject the report based on the optical method. For the reasons given in paragraph 2 (v.s.), the assessment by this method was also sometimes disputed.

In 1929 Dr. Dunnicliff undertook the detailed examination of the phloroglucinol method and standardised the conditions of test. I understand from him that the old "fibre count" method has been discarded, that a Spence and Krauss weight-length method is now officially authorised at the Custom House Laboratories in India, and that complaints are now comparatively rare.

In disputed cases the phloroglucinol method, as set forth by Dunnicliff and Suri (*loc. cit.*), is used at the Control Laboratory of the Central Board of Revenue. They recommend a standard temperature of 35° C., and they define standard conditions which will enable reproducible determinations to be made, accurate to about *plus* or *minus* 1 per cent. This is clearly a great advance on methods hitherto available, and it is satisfactory to know that it has become the official method for confirming tariff duty payable in India.

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Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

COUNTY PALATINE OF LANCASTER

ANNUAL REPORT OF THE COUNTY ANALYST FOR THE YEAR 1931

THE total number of samples examined during the year was 5448, of which 5146 (3010 formal and 2136 informal) were foods and drugs; of these, 139 were returned as adulterated.

MILK.—One hundred and twelve (3·7 per cent.) of the 3010 samples examined were adulterated.

"APPEAL-TO-COW" SAMPLES.—The earliest reference to "appeal-to-cow" samples appears to be that in the report of the Local Government Board (now the Ministry of Health) for 1879 in connection with Salford. "The Analyst states that if samples taken at the station correspond with former adulterated samples, he makes a point of seeing the cows milked and analyses a sample obtained in his presence, so as to leave no chance of an innocent person being convicted."

It has not been possible to determine exactly when the first sample was taken in the County of Lancaster, but complete records are available since the year 1903. Tables showing the composition of "appeal-to-cow" samples from that year until 1931 are published in this Report.

The Freezing-Point of Milk.—Since this work was started in the County Laboratory 211 samples of genuine milks have been examined. The determined freezing-point depression has varied between 0·530° C. and 0·561° C., with an average figure of 0·543° C. This figure agrees substantially with those found by all other observers whose work has been published, or which is personally known to the writer (*cf.* ANALYST, 1930, **55**, 423).

With regard to abnormal samples, in every case so far investigated the abnormality has taken the form of a greater depression rather than a smaller, so that, although the addition of a little water to an abnormal milk might pass on the evidence of the freezing-point alone (even this possibility is much reduced by the taking of "appeal-to-cow" samples), it is most unlikely, in fact, almost impossible, that a genuine milk would be suspected of being watered.

Mathieu and Ferré's Formula.—This denotes the sum of the weight of crystallised lactose and of the sodium chloride expressed as the (isotonic) equivalent of lactose. The value of this constant for most milks is said to be between 74 and 79, and to be reduced below 74 when any considerable quantities of extraneous water are present (*J.S.C.I.*, 1914, **33**, 214).

This method has been examined by various workers (Mathieu, *J.S.C.I.*, 1916, **35**, 613; Ferris, *J.S.C.I.*, 1917, **36**, 1245; Sirot and Joret, *J.S.C.I.*, 1919, **38**, 475A; Fonzes-Diacon, *J.S.C.I.*, 1919, **38**, 787A; and Joret and Radet, *B.C.A.*, 1927, 794B), who have found this suggested constant to vary more than had originally been supposed. Figures varying between 69·2 and 82·8 have been reported.

The "Cryolac Number."—P. Post (*B.C.A.*, 1926, 846B) has introduced what he terms the "cryolac number." This is an expression which is obtained by calculating the theoretical freezing-point due to the lactose and chlorides (calculated as common salt), both of which are determined chemically. Fiehe and Kordatzki (*B.C.A.*, 1928, 687B) found that the cryolac number accounted for 75 per cent. of the total freezing-point depression, and that it varied between 393 and 435, with a mean of 413.

The observed variation in the freezing-point, as between one genuine milk and another, is less than that in the case of the cryolac number, so that, in general, the former method is to be recommended. In cases where the freezing-point cannot be determined, however, the cryolac number may be of use, particularly for sour milks, as it takes into account the acidity of the sample.

CREAM CONTAINING GLYCERIN.—An informal sample, containing 4·7 per cent. of glycerin, was returned as adulterated. The addition of glycerin to food is not prohibited by the Preservatives Regulations, but it has been shown that in quantities of the order of 5 per cent. glycerin has little, if any, preservative action; in fact, the sample in question was slightly sour when received. The addition was probably made in a misguided attempt to improve the appearance of the article.

GRAVY BROWNING.—One sample, submitted as a browning for fish, was described on the label as follows: ". . . is new-laid eggs and golden toasted rusks."

It was found to contain not more than 2 per cent. of dried eggs, which must be regarded as unsatisfactory, in view of the statement on the label, and, more particularly in view of the colour of the sample, which might be thought to give support to the claims made.

Another sample contained 0·13 per cent. of ferric oxide, which might have been added as a colouring agent.

HEALTH SALTS (LIME JUICE AND SULPHUR SALTS).—A sample, described on the label as "Lime Juice and Sulphur Salts," was found to consist of a mixture of sugar, tartaric acid and sodium bicarbonate, with a small amount of sulphur. There was also present a small amount of essential oil of lime, but this was the only ingredient present that could be said to have any connection with lime juice. In view of the very considerable therapeutic value which is assigned to lime fruit, the description of this sample must be considered as unsatisfactory. The mixture did not even contain citric acid.

LEMONADE POWDER.—A sample, described as "lemonade powder," consisted of a mixture of cane sugar and tartaric acid, flavoured with oil of lemon; there was no citric acid.

ORANGE SQUASH ESSENCE.—A sample, which was described as "Orange Squash Essence" and was labelled "Pure Orange Squash to make 20 glasses of Orange Squash," consisted of a 20 per cent. solution of citric acid, which was flavoured with the pulp and essential oil of orange. The composition of this sample, compared with those of two samples, sold respectively as "concentrated orange juice" and as "orange squash," was as follows:

	Total solids Per Cent.	Citric acid Per Cent.	Proportion of citric acid to total solids Per Cent.
Orange squash essence ..	23·4	22·7	97·1
Concentrated orange juice ..	67·2	6·3	9·4
Orange squash	41·6*	2·1	5·1

* Contained added cane sugar.

From these figures and the general character of the sample, it is obvious that this article was, for the most part, an artificial mixture intended to counterfeit the natural article.

JAM.—The percentage of total soluble solids in the 65 jams examined has varied between 67·1 and 75·4 per cent., with the exception of one sample, which was as low as 63·7 per cent., as determined by the refractometer. In all cases the amount of insoluble solids has also been determined, and the results obtained, together with others obtained during the year 1930, are given in the following table:

INSOLUBLE SOLIDS IN JAM, PER CENT., 1930–31

	Number	Average	Highest	Lowest
Blackcurrant	19	2·17	2·98	1·29
Strawberry	44	1·19	2·28	0·52
Raspberry	23	2·14	3·00	0·72
Apricot	6	1·04	2·76	0·44
Damson*	13	0·81	1·73	0·40
Red plum	2	—	0·51	0·48

* Without stones.

ZINC IN CANNED LOBSTER.—A sample of canned lobster contained zinc to the extent of two-thirds of a grain per pound, calculated as metallic zinc. There was no indication that the zinc had been derived from the container. Traces of copper are not infrequently present in lobster, but so large an amount of zinc as this is unusual.

TURMERIC IN PEPPER.—One sample of pepper was found to contain a small amount of turmeric. None of the other 801 samples examined during the last six years has contained more than a trace of turmeric.

ACETIC ACID AS "PURE VINEGAR."—A sample of diluted acetic acid, coloured with caramel, was labelled as "An unfermented vinegar for household use." It might very well be argued that this is a contradiction in terms, the word "vinegar"—originally applied to sour wine, which is now described as wine-vinegar—being usually given to a fermented product. For some time now diluted acetic acid has been described by some persons as "Pure Vinegar"; they have even gone so far as to claim that such a "Pure Vinegar" is better, as it does not include the "Impurities" usually present in ordinary vinegar. An analogous proposition would be the description of diluted alcohol as "Pure Wine," and it is to be feared that the introduction of the term is merely an attempt to pass off an inferior article on the reputation of a better.

G. D. ELSDON.

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

LIABILITY OF MANUFACTURER FOR INJURIOUS DEFECTS IN HIS PRODUCTS

M'ALISTER OR DONOGHUE (PAUPER) *v.* STEVENSON

IN this case the House of Lords, by a majority of three to two (Lord Atkin, Lord Thankerton and Lord Macmillan; Lord Buckmaster and Lord Tomlin dissenting), allowed the appeal from a judgment of the Second Division of the Court of Session in Scotland, which, by a majority of three to one, had reversed the decision of the Lord Ordinary (Lord Moncrieff). Judgment was given on May 26th, 1932.

The appellant, a shop assistant, claimed £500 damages from the respondent (a manufacturer of aerated waters), for the injurious effects alleged to have been caused by the presence of a dead snail in a bottle of ginger beer manufactured by the respondent. The bottle was of dark opaque glass, so that its contents could not be ascertained by inspection, and was closed with a metal cap.

It was agreed by counsel on each side that the English and Scots laws on the subject were identical.

Lord Atkin, in delivering judgment, said that the question was whether, as a matter of law, the respondent owed any duty to the appellant to take care. He pointed out that in English law there must be, and was, some general conception of relations giving rise to a duty of care, of which the particular cases found in the books were but instances. But acts or omissions which any moral code would censure could not, in a practical world, give a right to every person injured by them to demand relief. Rules of law had arisen which limited the range of complaints and the extent of their remedy. Reasonable care must be taken to avoid acts or omissions which one could reasonably foresee would be likely to injure one's neighbour. In law one's neighbour seemed to be persons who were so closely and directly affected by one's act that one ought reasonably to have them in contemplation when directing one's mind to the acts or omissions which were called in question. That appeared to him to be the doctrine in *Heaven* v. *Pender* (11 Q.B.D., 503, 509), as laid down by Lord Esher, when it was limited by the notion of proximity, introduced by Lord Esher himself, and by Lord Justice A. L. Smith in *Le Lievre* v. *Gould* (1893, 1 Q.B., 491).

With that necessary qualification of proximate relationship, he thought that the judgment in *Heaven* v. *Pender* expressed the law of England. No doubt cases would arise where it would be difficult to determine whether the contemplated relationship was so close that the duty arose. But he could not conceive any difficulty in the class of case before the Court. A manufacturer put up an article of food in a container, which he knew would be opened by the actual consumer. There could be no inspection by any purchaser, and no reasonable preliminary inspection by the consumer. Negligently, in the course of preparation, he allowed the contents to be mixed with poison. It was said that the law of England and Scotland was that the poisoned consumer had no remedy against the negligent manufacturer. If that were the result of the authorities, he would consider the result a grave defect in the law. Not only would the consumer have no remedy against the manufacturer, but he would have none against anyone else for negligence; and, except in the case of a consumer, who was also a purchaser, there would be no contract and no warranty of fitness· and if a specific article were purchased under its patent or trade name, there would be no warranty protecting the purchaser-consumer. There were other articles, such as many forms of goods sold for cleaning purposes, to which the doctrine supported by the decision below would apply. The manufacturer knew that the articles would be used by persons other than the actual ultimate purchaser—namely, by members of his family, his servants, and, in some cases, his guests. He did not think so ill of their jurisprudence as to suppose that its principles were so remote from the ordinary needs of civilised society and the ordinary claims it made on its members, as to deny a legal remedy where there was so obviously a social wrong.

In his opinion, several of the authorities supported the view that, in such a case as the present, the manufacturer owed a duty to the consumer to take reasonable care in the preparation or putting up of the products, when the absence of such reasonable care was likely to result in injury to the consumer's life or property. It was a proposition which, he ventured to say, no one in Scotland or England, who was not a lawyer, would for one moment doubt. It would be an advantage to make it clear that the law in this matter, as in most others, was in accordance with sound common sense. He thought that the appeal should be allowed.

Lord Thankerton and Lord Macmillan agreed that the appeal should be allowed.

SALE OF A POISONOUS DISINFECTANT BY GROCERS

Council of the Pharmaceutical Society of Great Britain *v.* Brown

On May 9th, a Divisional Court of the King's Bench Division dismissed the appeal of the Council of the Pharmaceutical Society against a judgment given by Judge Higgins at Brentford County Court in favour of the defendant (Analyst, 1932, 30).

The proceedings were instituted under Sec. 15 of the Pharmacy Act, 1868, which provides that any person not being a duly registered pharmaceutical chemist, or chemist and druggist, who sells a poison to which the Acts apply, shall be liable to a penalty not exceeding £5; and under Sec. 12 of the Pharmacy Act, 1852, which provides that all penalties under the Acts may be recovered as a civil debt in the County Court.

An inspector in the employment of the appellants had bought from the respondent, a grocer, a bottle of Izal in a bottle described as the "Universal Pack," and analysts were called at the County Court trial to prove that the article contained more than 3 per cent. of homologues of carbolic acid. The County Court Judge held that if, as in this instance, the preparation was sold with a notice that it was intended for use in agriculture or horticulture, the section had been complied with.

Mr. Justice Acton, delivering judgment, said that the crucial question was whether the preparation came within the exception contained in the latter part of the definition in the Schedule. The qualification covered by the words exclusively, distinctively and definitely could not be introduced. It was sufficient for the defendant to show that the article had been prepared for some purpose in connection with agriculture and horticulture. He need not show that it was exclusively so prepared, or that it could not be used for any other purpose. It was argued for the appellants that the label on the bottle was a pretence which did not in any sense represent the true purpose for which the article was made up and sold. But there was ample evidence that the preparation had been sold for many years for agricultural and horticultural purposes, the only difference being that, until recently, it had been packed in tins instead of bottles. He considered, therefore, that the appeal should be dismissed.

Mr. Justice Talbot gave judgment to the same effect.

EGG BAKING POWDER

Alleged False Label

On May 31st, at Saltash Police Station, a manufacturing firm was summoned, under Sec. 30 of the Sale of Food and Drugs Act, 1928, for having sold an article—Egg Baking Powder—which was falsely described on the label. Mr. C. Knight, who prosecuted on behalf of the Cornwall County Council, said that the major point of the prosecution was that there was no egg in the sample, and that the label was therefore fraudulent; secondly, if there were 1 per cent. of egg in the sample, which was not agreed by the prosecution, the label was still fraudulent, and the submission of the prosecution was that 1 per cent. would not be sufficient to justify the label. The County Council had a duty to the retailer and a duty to the public in that it had to see that they were not misled into buying that for which they had not asked. The certificate of the Public Analyst, Dr. H. E. Cox, said that the sample was coloured baking powder of satisfactory composition, but, as it did not contain any egg, was not correctly described as Egg Baking Powder.

Dr. Cox, giving evidence, said that the powder contained 67 per cent. of cereal and about 33 per cent. of a mixture containing bicarbonate of soda, tartaric acid, acid sodium pyrophosphate, and a trace of dye. He found 3·5 per cent. of proteins, 0·58 per cent. of fat, and 0·02 per cent. of organic phosphoric acid; he was of opinion that these were all attributable to the cereals, and he found no definite evidence of egg. He agreed that there might be 0·1 or 0·2 per cent., but regarded 1 per cent., which was suggested by the Government Chemist, as an over-estimate, as the amounts of protein, fat and organic phosphorus were, within experimental error, the same as those he found in baking powder of the same manufacture not alleged to contain egg. An experiment was shown demonstrating that 1 per cent. of egg in such a mixture could be separated by flotation, whereas none could be so separated from this sample. If the powder did, in fact, contain 1 per cent. of dried egg, a cake made in accordance with the directions on the label would contain only about 1/10,000th part of egg. In his opinion, a powder labelled "Egg Baking Powder" ought to contain quite a substantial proportion of egg.

Mr. Wolferstan, defending, referred to the case heard before the Saltash Bench last August (Analyst, 1931, **56**, 661), and said that the manufacturers had recalled and re-labelled the product "Egg Baking Powder," and considered that they had done everything to keep within the four corners of the Act.

A certificate from the Government Chemist was produced, which stated that the sample consisted of baking powder coloured yellow, containing a small proportion of dried egg, which had been identified microscopically, and expressed the opinion that it contained about 1 per cent. of dried egg.

Mr. T. Tickle, County Analyst for Devon, said that he had analysed the sample and found commercial dried egg yolk amounting to 0·75 per cent.; he had since seen the manufacturers' formula, which showed 1 per cent. of dried egg yolk. He would not expect nutritive value in baking powder, and, if the powder were called egg baking powder, he would not expect nutritive value in it.

The manager of the defendant's firm stated that the recipe included a definite quantity of dried yolk of egg, and that he superintended the manufacture.

After a retirement the Bench announced that they must convict, fined the defendants £5, and ordered them to pay 5 guineas costs.

The National Physical Laboratory

REPORT FOR THE YEAR 1931*

THE Report for 1931 follows the same general arrangement as that for 1930 (ANALYST, 1931, **56**, 661). A general survey of the work is made in the Report of the Executive Committee; a comparison of tests for 1929, 1930 and 1931 follows, and a list of published papers for 1932, official and unofficial, occupies some 11 pages. The Reports of the Superintendents of the different departments deals with details of the work, and a few investigations only can be mentioned here. A detailed description of the new Physics building is given.

GOVERNMENT RESEARCH.—Among the special investigations, the study of the crystalline structure of teeth was continued, in conjunction with the Dental Disease Committee of the Medical Research Council; the constituents of both enamel and dentine have been found to be identical with that of apatite, but the crystals are arranged at random in the dentine, and with a marked selective orientation in the enamel, so that the [001] directions of the crystals are inclined at an angle of approximately 20 to the normal to the surface of the tooth in human teeth, but the [001] of canine teeth coincides with the normal to the surface. *X*-ray photographs showed that the dentine contains much more amorphous material than the enamel.

STANDARDS OF MEASUREMENT.—Work towards the establishment of international standards of candle-power for work at higher colour temperatures than that corresponding with the colour of the primary unit, has involved measurement by the national laboratories of France, Germany, United States, and Great Britain, of the transmission of 4 blue glasses supplied by the Reichsanstalt, Berlin, which, used with a carbon-filament lamp of colour temperature 2,080° K, give light of colour temperature 2400° K, that is, approximately the colour temperature of a tungsten-filament vacuum lamp. A discussion of the measurements resulted in agreement that the spectrophotometric method of measurement gave the most concordant results, and that this method would be accepted and standards adjusted accordingly.

RELATIVE PERMEABILITY OF VARIOUS MATERIALS TO WATER VAPOUR.—Waxed paper was found to be of low permeability, compared with treated (soaked in medicinal paraffin) and untreated brown paper; calico treated with mutton fat had a permeability of one-third that of treated brown paper. Parchment paper is about 4 times as permeable as treated brown paper, so that, commencing with the lowest, the order of permeability is: White waxed paper, calico impregnated with mutton-fat, brown paper soaked in paraffin, and parchment paper.

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* Department of Scientific and Industrial Research. H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 15s. net.

EFFECT OF TEMPERATURE ON THE RELATIVE "SPREADABILITY" OF BUTTER.—Extrusion under measured pressure through a sharp-edged orifice was adopted as a means for comparative tests. Butters of different origin and blends of butter were tested over a range of temperatures. Other points investigated were (*a*) the effect of "working" the sample, (*b*) the effect of prolonged storage at temperatures well below freezing-point, and (*c*) the effect of storage at temperatures near the freezing-point.

OPTICS.—*Colour Measurement and Standardisation.*—The agreement reached at the meeting of the International Commission on Illumination on the subject of colorimetry accepts the principle developed at the Laboratory (ANALYST, 1931, **56**, 662), with certain changes in detail. The "basic stimulus"* of the system finally selected is an "equal energy spectrum," and the primaries—necessarily hypothetical stimuli—are so chosen that all colorimetric quantities are expressible by positive numbers. The "luminosity factors" of the primaries are respectively 0 : 1 : 0. The distortion of the colorimetric scales, *i.e.* the variation in the significance of given small changes in the colorimetric co-ordinates in different parts of the field, is as small as possible. To the three homogeneous radiations adopted as the primaries of the laboratory system, and to a heterogeneous stimulus from a specified lamp and filter combination of very similar colour and energy distribution to the N.P.L. standard white are ascribed definite co-ordinates, and the list of spectral coefficients defining the proposed standard observer has been transformed from the laboratory to the new system and adopted as the international standard. The laboratory instruments have been re-calibrated in terms of the new system, but no alteration is involved in the experimental procedure to be followed by practical colorimetrists, but only a reduction of results, and an explanatory paper is being prepared to facilitate the use of the system.

METROLOGY.—*Volumetric Glassware and Hydrometers.*—The drafting of standard specifications for glassware and for the testing of milk and milk products has been undertaken by the glassware sub-committee of the Dairy Research Committee of the Empire Marketing Board, and a very extensive series of experiments has been necessitated. The work on the surface-tension of milk has resulted in the average value at ordinary room temperature being taken as 45 degrees per cm., and variations are unlikely to exceed 5 degrees per cm. Proposals for a standard lactometer are being prepared in which, when the above figure for the surface tension is used as a basis for the standard, errors due to variation of the tension should not exceed 1 in 10,000. Standardisation of standard specific gravity hydrometers has been carried out in conjunction with surface-tension measurements over a range of specific gravity from 0·9000 to 1·300.

METALLURGY.—*Study of Special Alloy Systems.*—Much attention has been given to methods of melting aluminium alloys, and of removing dissolved gases, including bubbling of nitrogen through the metal (which is often effective), introduction of a volatile chloride, *e.g.* titanium chloride or carbon tetrachloride, and a combination of the two methods. Final conclusions have not yet been reached.

* This term has recently been suggested by I. G. Priest, of the Bureau of Standards, to denote the stimulus which is colorimetrically matched by numerically equal "quantities" of the primaries of a trichromatic system. In the system hitherto employed in the Laboratory the "primaries" are homogenous radiations of wave-lengths 0·700μ (red), 0·5461μ (green), and 0·04358μ (blue), and the "basic stimulus" is the radiation given by the particular lamp and filter combination hitherto known as the National Physical Laboratory standard white light.

Work on the age-hardening and rolling properties of some magnesium alloys has necessitated the use of a flux to protect the metal against the action of the air, and crucibles of austenitic chromium-nickel steel had to be used. The study of magnesium-manganese alloys has been begun; so far, the maximum of manganese possible to introduce into the alloy is 5 per cent. An alloy of magnesium containing 0·15 per cent. of beryllium has been prepared.

Study and Improvement of Methods of Metallurgical Analysis.—The testing of high-chromium, high-nickel rust-resisting steels used in the second heightening of the Aswan Dam has shown some slight modifications in methods to be desirable. The effects of impurities in copper have involved intricate analyses, and the observations of Hampe on the constitution of minute residues of antimonates of bismuth remaining insoluble after the solution in nitric acid of copper containing antimony, bismuth and oxygen, have been confirmed. To facilitate the analysis of alloy steels, an apparatus for determining sulphur has been installed.

British Standardised Steel Samples.—Accurately standardised steels by means of which analytical methods can be tested have been prepared, in collaboration with District Authorities representative of the local university or equivalent institution, and of the works or commercial laboratories of the district. No samples are sent out until final values have been accepted after substantial agreement between all the analysts and a definite limit of possible error can be stated. The standards available, each analysed for one element (impurity) only, are:

No. 1. .. Sulphur (S=0·027 per cent.).
No. 2. .. Sulphur (S=0·071 per cent.).
No. 3. .. Phosphorus (P=0·029 per cent.).
No. 5. .. Carbon (C=0·65 per cent.). Acid O.H. steel.
No. 6. .. Carbon (C=0·10 per cent.). Basic O.H. steel.
No. 8. .. Carbon (C=0·27 per cent.). Acid O.H. steel.
No. 9. .. Carbon (C=1·09 per cent.). Acid O.H. steel.
No. 11. .. Manganese (Mn=0·69 per cent.). Acid O.H. steel.
No. 12. .. Cast iron standard sample (Si=2·22 per cent., P=1·14 per cent., Mn=0·50 per cent., S=0·075 per cent.).

D. G. H.

Ministry of Agriculture and Fisheries

AGRICULTURAL PRODUCE (GRADING AND MARKING) ACT, 1928

STATUTORY RULES AND ORDERS, 1930, No. 370

Agricultural Produce (Grading and Marking), England, Order No. 370 (Analyst, 1931, **56**, 108) has been superseded by S.R.O., No. 458, of 1931 (Fruits), and No. 442, of 1931 (Vegetables). These orders are obtainable from H.M. Stationery Office, price 1d. each. No. 458 is in terms similar to No. 370, but includes, in addition to the fruits therein named:

Select raspberries and redcurrants
Select dessert cherries
Select Morello cherries
Select cultivated blackberries
Select redcurrants

The strength of syrup in which they are to be packed remains the same, *viz.* 40 per cent. for plums and 45 per cent. for the others.

Order No. 442 (Vegetables) defines the quality of select beans (whole and sliced), beetroots, carrots (whole), celery (hearts), peas, new potatoes, spinach, turnips (whole), macedoine of select vegetables; it also gives a list of the varieties of plums, apples, cherries and peas which shall be used, and an experimental schedule of minimum fruit weights and net weights.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Non-Homogeneity of Casein. Fractionation by means of Ammonium Chloride. E. Cherbuliez and M. L. Schneider. (*Helv. Chim. Acta*, 1932, **15**, 597–609.)—By fractional precipitation of a solution of casein in dilute sodium hydroxide or ammonia solution by means of ammonium chloride, it is shown that casein consists of two components, termed α- and β-caseins, which are respectively insoluble and soluble in the ammonium chloride solution. The proportion of the β-form, which is highly hygroscopic, is between five and eight times that of the α-form. The percentage compositions of the two fractions and of the original casein are as follows:

	C	H	N	S	P
Casein ..	52·45	7·21	15·59	0·64	0·84
α-Casein ..	52·52	7·12	15·25	0·61	0·72
β-Casein ..	52·60	6·88	15·34	0·75	2·32

That the separation is not accompanied by hydrolysis of the casein is shown by the facts that the neutralisation equivalents of the α- and β-forms differ little from that of casein, and that the proportion of formol nitrogen is higher in casein than in either α- or β-casein. The optical rotation of a 1 per cent. solution in 0·01 *N* NaOH is $[\alpha]_D = -111°$ for each of the three compounds.

α-Casein resembles casein in properties, whereas the β-form shows appreciably different behaviour, its solubility relations, for instance, approaching more nearly those of the globulins than those of casein. β-Casein (1 part) dissolves rapidly in aqueous pyridine (200 parts) at the ordinary temperature, whereas α-casein is almost insoluble in this solvent. From its 3 per cent. solution, α-casein, like casein itself, is coagulated by rennet to give a dense curd, whilst the β-modification yields only a slight coagulum without markedly altering the fluidity of the liquid.

T. H. P.

Prediction of the Extract of Malt by Bishop's Barley Formula. W. J. Mitchell. (*J. Inst. Brewing*, 1932, **38**, 241–244.)—Bishop (*J. Inst. Brewing*, **1930**, **36**, **421**) has shown that, for Plumage–Archer barleys of one strain, the extracts of the malts obtained therefrom can be predicted from the equation, $E = 110{\cdot}1 - 11{\cdot}2\,N + 0{\cdot}18\,G$, where E is the extract in brewers' lbs. per quarter of dry malt, N is the percentage of nitrogen in the dry barley, and G is the weight in grms. of 1000 corns of the dry barley. This equation is applicable to barleys which have been grown under widely varying conditions (soil, weather, manuring). Moreover, by suitable modification, the equation may be rendered valid for barleys of another variety; *e.g.* for Spratt–Archer barley, $E = 110{\cdot}6 - 11{\cdot}2\,N + 0{\cdot}18\,G$.

The author has collected the nitrogen-contents and 1000-corn weights of 279 samples of kiln-dried barley, mostly of second grade and representative of the production of most of the barley-growing districts of Scotland and Northumberland for a single season, together with the mean values calculated by taking into account the weights of the different lots. These mean values are, for the dry barley: nitrogen, 1·62 per cent., and 1000-corn weight, 40·73 grms. During the corresponding malting season, the brewers' extract was determined for each of 126 samples of malt made from barleys of the same origin. Application of Bishop's Plumage-Archer formula to the mean figures for the barleys gives, for the predicted extract of the resulting malt, 99·3 lbs. per quarter, whereas the actual mean value for the malts examined is 98·9 lbs. It is, therefore, suggested that subtraction of 0·4 (*i.e.* 99·3–98·9) from the right-hand side of this equation will yield a formula allowing of the prediction of the extracts of malts made from Scotch barley of second grade.

Further confirmation of the usefulness of Bishop's formula is obtained from the results furnished during a period of six years by 20 samples of high-grade Scotch barleys of known history. Each of these barleys, which differed widely in regard to conditions of growth, was malted in a 20-quarter experimental malting. The average figure found for the predicted extract of the malt was 99·7 lbs., and the average actual extract of the malt, determined by the standard laboratory method, was 99·8 lbs. per qr. With only three of the samples is the agreement between actual and calculated extract unsatisfactory. In two of these three cases, the malting losses were abnormally high, so that Bishop's formula becomes invalid, but the third case is not explainable in this way. The formula may also be used when a method other than the standard method is employed for determining the amount of extract yielded by the malt, provided that the "equation constant" (110·1) is suitably changed. T. H. P.

Colorimetric Estimation of the *p*H Value of Wort or Beer. P. Kolbach. (*Wochenschr. f. Brauerei*, **1932, 49,** 81–85.)—The results obtained when the *p*H of wort or beer is measured by the ordinary comparator method are subject to errors due to the following causes: (1) The colour of the indicator (especially if two-colour) may be not quite the same in wort or beer as in a buffer solution of similar *p*H value. (2) The indicator may be adsorbed to some extent by the colloids of the wort or beer, and its colour may be affected by oxidising or reducing substances present. (3) The salts in the buffer solution used in the colour comparison have an influence on the colour not exerted by the wort. The first two of these sources of error are avoidable by eliminating the cells containing water and untreated wort, respectively, a mixture of the sample, indicator and buffer solution being matched against a mixture of sample, indicator, and water in similar proportions. The indicator is then in a similar medium in each of the two mixtures, except for the salts of the buffer solution; this "salt error" may be reduced by using 0·1 *N* sodium chloride solution, instead of water, in the other mixture.

The procedure to be followed is described in detail. The indicators recommended are: bromocresol green (*p*H 4·0 to 4·8), methyl red (4·8 to 5·6) and bromocresol purple (5·6 to 6·4), and use is made of a series of succinate buffers covering the total range of *p*H values with steps of 0·2. The salt corrections, which are given for the three indicators and for worts of various specific gravities and various degrees of attenuation, usually amount to only 0·05 or 0·1. The results obtained by this method are correct to within 0·1. T. H. P.

"Ketone Rancidity" of Fats. I. New Method of Detection. K. Täufel and H. Thaler. (*Chem. Ztg.*, 1932, **56**, 265–266.)—The following reaction, based on the formation of red condensation products of salicylaldehyde with higher aliphatic ketones, is capable of detecting the ketone rancidity of fatty products, such as butter and margarine, in its early stages:—From a 200-c.c. distilling flask, provided with a ground-in stopper and delivery tube, and charged with 180 c.c. of water and a few scraps of material to prevent bumping, 25 to 30 c.c. are distilled through a short Liebig condenser into a large test-tube. Pure salicylaldehyde (0·4 c.c.) is added to the distillate, which is vigorously shaken to give an emulsion. After the aldehyde has settled, all but about 4 c.c. of the water is poured away, the contents of the tube being then emulsified again. Two c.c. of pure sulphuric acid are then poured in a stream (not down the side of the tube) into the liquid, which is afterwards well shaken. When the tube is left at rest for a short time, the salicylaldehyde separates, leaving a lower milky layer. This blank experiment should give an aldehyde layer with no more than a very faint pink (usually a faint yellow) colour. Into the water (about 150 c.c.) remaining in the distilling flask, 10 grms. of the fat to be examined are introduced by means of a long funnel. The subsequent procedure is that followed in the blank experiment. If the fat contains even traces of ketone, the layer of salicylaldehyde separating from the sulphuric acid shows a distinct pink colour. As the intensity of the coloration usually increases if the liquid is heated for a short time, it is advisable, especially when only a weak colour reaction is given, to place the tubes from both the blank and the actual experiment for 15 minutes in a boiling water-bath.

The colour given, under the above conditions, is orange with acetone, and deepens as the carbon-atom chain of the ketone lengthens, so that methyl-nonyl-ketone gives an intense raspberry-red colour. The reaction is not given by aldehydes or by those aromatic ketones which have been examined. A distinct coloration is obtained with coconut fat (10 grms.) to which methyl-nonyl-ketone, in the proportion of 1 to 500,000, has been added. The apparatus must be scrupulously cleaned with boiling caustic alkali solution, and then with hot nitric-sulphuric acid mixture before use, and the employment of water prepared by electro-osmosis or of rubber or cork connections must be avoided. If commercial salicylaldehyde is to be used, its preliminary purification by means of the bisulphite compound is necessary. T. H. P.

Philippine Rice Oil. (Ramai variety.) A. O. Cruz, A. P. West and V. B. Aragon. (*Phil. J. Sci.*, 1931, **48**, 5–13.)—Rice bran (polishings) contains oil which readily hydrolyses. Ramai rice is a Philippine lowland variety, with rather large grains; the dry bran contained about 18 per cent. of oil, which, when clarified, was dark brown with a greenish tinge, and had the following characteristics:—Sp.gr., 30°/4° C., 0·9059; n_D^{30}, 1·4662; saponification value, 185·9; iodine value (Hanus), 99·3; acid value, 42·2; unsaponifiable matter, 4·0 per cent.; saturated acids (corrected), 19·9; and unsaturated acids (corrected), 69·7 per cent., with iodine value 124·7. The saturated and unsaturated acids occurring as glycerides were separated, and by application of the lead salt and ether method, by the preparation of the bromine derivatives of the unsaturated acids, and by esterification of the saturated acids the composition (expressed as glycerides) of the oil was calculated as oleic, 45·3; linolic, 27·6; myristic, 0·1; palmitic, 16·9; stearic, 2·6; arachidic, 0·5; and lignoceric acid, 0·9; and unsaponifiable matter, 4·0 per cent. This is very similar to the composition of kapok and cottonseed oils, and rice oil appears suitable for similar purposes, but, owing to the difficulty of expression, would appear to need extraction plant for its commercial production. D. G. H.

Composition of Philippine Talisay Oil from the Seeds of *Terminalia Catappa*. A. O. Cruz and A. P. West. (*Philippine J. Sci.*, 1932, **48**, 13–19.)—*Terminalia catappa*, L, is a tree reaching 25 metres in height, which grows in the Philippines near the sea shore, and has seeds with edible kernels yielding talisay oil, known in India as Indian almond oil. The whole seeds contained about 3 per cent. of oil, or about 52 per cent. in the kernels, and the oil had specific gravity at 30° C./4° C., 0·9046; $n_D^{30°}$ C., 1·4644; saponification value, 193·2; iodine value (Hanus), 75·4; unsaponifiable matter, 0·54 per cent.; acid value, 2·5; saturated acids (corrected), 32·62; unsaturated acids (corrected), 61·01 per cent., with iodine value 122·9. The saturated and unsaturated acids were separated, and the composition (expressed as glycerides), eventually calculated as oleic, 40·85; linolic, 22·91; myristic, 1·00; palmitic, 28·47; stearic, 3·99; and arachidic acid, 0·75; and unsaponifiable matter, 0·54 per cent. D. G. H.

Rapid Method for the Determination of the Amount of Sodium Nitrite in Pickling- and Preserving-Salt. J. Peltzer. (*Chem. Ztg.*, 1932, **56**, 383.)—The sample (10 grms.) is dissolved in 150 c.c. of water and neutralised, if necessary, to phenolphthalein. It is then boiled with 15 c.c. of 0·1 *N* sulphuric acid and a little pumice until the nitric oxide liberated according to the equation, $3NaNO_2 + H_2SO_4 = Na_2SO_4 + NaNO_3 + 2NO + H_2O$, is removed, and the excess of acid is then titrated with 0·1 *N* alkali (1 c.c. acid ≡ 0·0103515 grm. $NaNO_2$). Qualitative or quantitative tests for the nitrate formed in this reaction may also be applied. Thus, an aliquot portion of the solution is mixed with three times its volume of concentrated sulphuric acid, and the cooled mixture (nitro-sulphonic acid) is shaken with brucine, the red colour being then matched with that given by a standard solution treated in a similar way. J. G.

Identification of Corynanthine. J. Sidvadjian. (*J. Pharm. Chim.*, 1932, **124**, 352, 353.)—The following reactions appear to be similar for yohimbine and its optical isomer, corynanthine. In Fröhde's reaction, both dissolve to give a blue colour; with Mandelin's reagent a violet colour, and with Meillère's reagent, also, (dilute sugar solution and concentrated sulphuric acid) a violet colour is formed. Further, if a few mgrms. of vanillin or of piperonal are added to a solution of either substance, and concentrated sulphuric acid is then poured in, a violet colour is formed. An addition of a few mgrms. of corynanthine, or of yohimbine, and of the same quantity of chloranil to 2 c.c. of epichlorhydrin gives, on boiling, a brown coloration, and the addition of concentrated nitric acid to the cooled liquid changes the colour to cherry-red. D. G. H.

New Reaction of Aconitine and of the Total Alkaloids of Aconite. C. Brugeas. (*Ann. Falsificat.*, 1932, **25**, 147–149.)—Aconitine itself gives a red-violet coloration in Monti's reaction (sulphuric acid and resorcinol heated on a water-bath), but, when made alkaline with strong sodium carbonate solution, the liquid becomes colourless with a blue fluorescence. If, however, the residue extracted from a preparation of aconite (prepared by Ogier's modification of the Stas method) is used, the red-violet colour changes, on rendering the solution alkaline, to an intense purple with green fluorescence. The shade of purple varies with the concentration of the alkaloid, but the fluorescence persists, although gradually fading on standing. A positive reaction is indicative of the presence of the total aconite alkaloids. D. G. H.

Biochemical

Halibut-Liver Oil as a Source of Vitamin *A*. J. A. Lovern. (*Nature*, 1932, **129**, 726.)—The author has confirmed the fact, reported by other workers, that the liver oil of the halibut (*Hippoglossus vulgaris*) is a very rich source of vitamin *A* (of the order of 50 to 100 times as rich as cod-liver oil). All potencies from 30 blue units (0·2 c.c. of 20 per cent. solution) up to 1600 blue units have been observed, but not all samples of halibut-liver oil were found to give such high values, and this irregularity appears to be the rule and not the exception. Therefore, if halibut-liver oil is to become of commercial value as a ready-made vitamin *A* concentrate, as is hoped, it is necessary to know something of these fluctuations, whether they are seasonal, etc., especially as halibut-liver oil cannot be obtained by steaming the livers, but needs the more expensive process of solvent extraction. A series of experiments on this problem of the excessive fluctuations in vitamin *A* potency of halibut-liver oil is being carried out, and attempts will be made to find the seasonal effects (if any), and the influence of the diet of the fish concerned. P. H. P.

Sparing Action of Fat on Vitamin *B*. II. Rôle played by Melting-Point and Degree of Unsaturation of Various Fats. H. M. Evans and S. Lepkovsky. (*J. Biol. Chem.*, 1932, **96**, 165–177.)—It has been previously shown by the authors (*J. Biol. Chem.*, 1929, **83**, 269) that the liberal inclusion of fat in the diet will enable an animal to withstand for many weeks the withdrawal or omission of the antineuritic vitamin *B*, and that in the presence of fat more growth will occur at any definite level of vitamin *B* than with a fat-free diet. The effectiveness of lard and cottonseed oil was reported. It was thought important to determine whether the sparing action of a fat was in any way related to its physical properties, such as melting-point and degree of unsaturation. Samples of cottonseed oil, perilla oil, coconut oil and lard were used, also some synthetic, some hydrogenated, and some partly hydrogenated samples. It was found that, provided a fat melts near body temperature, neither its precise melting-point nor the degree of saturation plays an important rôle in the remarkable ability to spare the amount of vitamin *B* required for any definite growth performance. Fats melting at or above 62° C. are very poorly absorbed by the rat, and do not exhibit the above sparing action. Fats melting at 38° C. have just as effective sparing action as those which are liquid at room temperature. Fats almost saturated and possessing an iodine value of 8 are as effective as highly unsaturated fats with an iodine value of 187. To judge of the sparing action of any fat it was necessary to determine the degree of absorption. The food consumed was recorded, and the fat-content of the faeces was determined by extracting the faeces with hot benzene, and weighing the dried extract. P. H. P.

Sparing Action of Fat on Vitamin *B*. III. Rôle played by Glycerides of Single Fatty Acids. H. M. Evans and S. Lepkovsky. (*J. Biol. Chem.*, **1932, 96**, 179–188.)—It was felt that a deeper insight could be had into the problem by the use of fats consisting of the glycerides of single fatty acids. Attempts to carry out this project are described. Pure caprylic, capric, lauric, myristic, palmitic, and stearic acids, and their glycerides were prepared and tested on rats. The results show that, in the absence of vitamin *B*, some glycerides of single fatty acids permit better growth than do natural fats such as cottonseed oil. The glycerides differ among themselves, those of myristin and caprylin being more effective than the others. In the presence of vitamin *B*, however, natural fat is superior to any of the single glycerides The glyceride of stearic acid exerts no sparing action on vitamin *B*; in fact, the animals on this diet are in poorer condition than those on the fat-free diet. The poor growth performance of the animals receiving stearin can perhaps be attributed to the fact that it is very poorly absorbed, its bulk in the food causing a partial starvation. The glycerides of single fatty acids which permit better growth than do natural fats in the absence of vitamin *B*, do not possess properties in common, such as melting-point or length of chain. P. H. P.

Crystalline Vitamin *D*. C. E. Bills and F. G. McDonald. (*J. Biol. Chem.*, 1932, **96**, 189–194.)—In a recent communication, Bills, McDonald, BeMiller, Steel and Nussmeier (*J. Biol. Chem.*, **1931, 93**, 775) noted that the crystalline preparations of vitamin *D* reported by English and German workers had less antirachitic potency than certain non-crystalline preparations of their own. This observation has led to renewed and successful efforts to induce crystallisation in the active resinous products already described. It is shown that the potencies reported for several crystalline preparations of vitamin *D*, when translated into international units, reveal wide variation in antirachitic value. The known tendency of impure sterols to remain vitreous when cooled below their melting points suggested that crystallisation was but a matter of time. Several active resins of the same order of potency as several crystalline preparations, which had been put aside and protected from decomposition, were examined. Slow crystallisation was observed to occur in material which had stood for several weeks. At first only scattered islands of fine needles were seen; these gradually became rosettes, which, under magnification, resembled chestnut burrs. The older preparations were solid crystalline masses. It is significant that an activated ergosterol preparation, known to be impure, changed completely into a crystalline mass merely on standing. Therefore, under suitable conditions, a resinous preparation can pass into the crystalline state without change of purity. The crystalline state is evidence of relative, not absolute, purity in vitamin *D*. The best crystalline preparations as yet described are probably isomorphous mixtures containing a large percentage of inert material; they should be regarded as starting material for further fractionation. P. H. P.

Unsaturated Fatty Acids in Diet. II. H. M. Evans and S. Lepkovsky. (*J. Biol. Chem.*, 1932, **96**, 157–164.)—In studies on the physiological importance of fats to the animal organism, Evans and Lepkovsky (*J. Biol. Chem.*, 1929, **83**, 269) became convinced that progress could be made only when individual fatty acids were used; only when synthetic fats composed of single fatty acids are used in experimental diets will it be possible to accumulate a body of data which will lead to a better understanding of the rôle played by fats in the animal organism. The investigation now described is concerned with the rôle of single saturated fatty acids when vitamin *B* and, in fact, all the known vitamins, are adequately supplied. When glycerides of single fatty acids were used as the sole source of energy in the diet, certain phenomena akin to those obtained in studies on fat-free diets were shown, with some similarities, but some vital differences. The results show that animals do not thrive on diets which contain the essentials hitherto known (adequate amounts of protein, all of the known vitamins, and the essential inorganic constituents), but in which the energy requirements are met by the glycerides of saturated fatty acids. Glycerides of saturated fatty acids, when given as the sole source of energy, do not promote growth in the rat equal to that obtained with sucrose as the sole source of energy. Unsaturated fatty acid preparations containing fatty acids with more than one double bond markedly improve such diets. Oleic acid produces a very slight response, whereas linolic acid produces a marked response. The natural fats were superior in every case to the synthetic fats.

P. H. P.

Toxicological

Chromium Toxicology. Absorption of Chromium by the Rat. L. W. Conn, H. L. Webster and A. H. Johnson. (*Amer. J. Hyg.*, 1932, **15**, 760–765.)—Owing to the increasing use of "18–8" chromium-nickel steels for dairy machinery, the toxic effect of minute quantities of chromium has been investigated. Rats on chromium-free diet were housed in glass cages, in some cases with chromium-plated copper or chromium-plated nickel floor rods. In other cases rats were fed with milk previously kept for 3 hours at 60 to 65° C. in chromium nickel-steel containers, and, in still further experiments, they were fed with milk containing chromium lactate corresponding with 0·25, 0·5, 1, 10, 50, and 100 parts of chromium per million. The rats were then killed, and the alimentary tract was washed out and, together with the body, was dried and ashed, and the ash analysed. The chromium was determined by dissolving 1 to 5 grms. of ash in hot dilute hydrochloric acid, oxidising any chromium with sodium peroxide and boiling off the excess, diluting the cold solution to 200 c.c., centrifuging to throw down the calcium hydroxide, and determining the chromium in 100 c.c. of the supernatant liquid by Stover's diphenyl-carbazide method. (*J. Amer. Chem. Soc.*, **50**, 2363.) The only positive results were obtained with rats fed on milk containing the three largest amounts of chromium (10, 50 and 100 parts per million), which showed, respectively, 0·0023, 0·002 and 0·002 mgrm., which meant that only 0·03, 0·006, and 0·003 per cent., respectively, of the chromium given was retained. Since these small amounts were found in rats which had been given milk containing 20 to 200 times as much chromium as the largest amount found in milk kept in chromium-nickel-steel utensils, the menace to the public health from the use of such utensils is regarded as negligible. The presence of chromium in the food to the extent of 100 parts per million was found to have no ill effect on the general health or reproductive powers of the rats, and, further, it is not retained, but promptly and completely eliminated by the rat. In one case only of those in which the rats were in cages with chromium-plated floor-rods was any chromium found in the ash. D. G. H.

Bacteriological

Action of Penicillium on Artificial Silks. T. F. Heyes and H. S. Holden. (*J. Text. Inst.*, 1932, **23**, T79.)—It is already known that when a mixture of cotton and artificial silk becomes mildewed it is only the cotton which is attacked. Five types of artificial silk (acetate, nitrocellulose, viscose, stretch-spun and parallel-spun cuprammonium) were tested for resistance to five species of Penicillium:—*P. purpurogenum* var. *rubri sclerotium*, *P. pinophilum*, *P. lilacinum*, and two strains isolated from mildewed American cotton yarn and from black-stained mercerised cotton. About 1 grm. of each silk was wound round a glass reel, about 3 inches long, and sterilised in a plugged glass tube for 20 minutes in the presence of sufficient culture medium just to touch the silk. With each silk five series of cultures were made, the following liquids being used for wetting out:—Water, 1 per cent. asparagine solution, 1 per cent. ammonium nitrate solution, 1 per cent. potassium nitrate solution, 1 per cent. peptone solution. After inoculation with the Penicillium, growth was allowed to proceed for 3 months, after which, the cultures were removed, the silks were tested for breaking load, the fractured ends were examined microscopically, and the copper number was determined. The most resistant type of silk was the sample of acetate silk. Considerable tendering of a silk may take place through mould-growth, without the damage being visible microscopically. Stretching in the spinning process appears to confer some power of resistance on non-esterified silks. The same type of damage on any one sample was produced by the various species of Penicillium. The effects of asparagine, peptone, etc., vary, and the order of resistance of the silks, other than acetate, does not allow of generalisation. Full results are given in 8 tables. R. F. I.

Organic Analysis

Micro-Analytical Method for the Identification of Organic Substances. V. Staněk and T. Nemes. (*Chem. Ztg.*, 1932, **56**, 285–287.)—The method depends on the experimental determination of the "oxidation-value" of the substance in terms of potassium iodate, and comparison of this result with the theoretical value obtained from the sum of the iodate-oxidation equivalents of the individual atoms suspected to be present. The formula (14·268 × per cent. C + 42·466 × per cent. H + 81·207 × per cent. S − 9·167 × per cent. N − 5·351 ×

per cent. O) gives the theoretical percentage of potassium iodate required, and is deduced from the chemical equations expressing the oxidation of each of the individual elements. In the determination, 100 to 150 mgrms. of pure, powdered potassium iodate are weighed out to within 0·01 mgrm., and dissolved in 2 to 3 c.c. of warm concentrated sulphuric acid in a test-tube. A known weight of sample (1/10 to 1/30 of the amount of iodate taken) is weighed in a small glass dish, or if liquid, in a capillary tube, which is dropped into the test-tube and broken up with a glass rod, and the whole is heated in a sulphuric acid-bath at 190 to 205° C. (I_2O_4 forms at 230° C.). When no more gas is evolved, and the solution is colourless, it is cooled, washed with 50 c.c. of water into 100 c.c. of water in a flask, and the mixture is then boiled in the presence of a little pumice until all the free iodine is removed. The excess of iodate in the colourless solution is then titrated after addition of 1 grm. of potassium iodide, by means of sodium thiosulphate solution, with starch as indicator. The error in oxidation value for substances which are easily attacked (*e.g.* carbohydrates) is about ± 0·5 per cent., but volatile or more resistant substances (*e.g.* naphthalene, picric acid, osazones, halogen and sulphonated derivatives and hydrochlorides) give unreliable results. Ions which interfere with the iodate titration should, of course, be absent. It is suggested that in certain cases the iodine should be removed by distillation and collected and titrated, and it is also often necessary to determine the ammonia formed from any nitrogen present by distillation, and to apply confirmatory tests (*e.g.* m.pt.) to the original substance. J. G.

Method of Determining (Aromatic) Aldehydes, based on Cannizzaro's and Claisen's Reactions. L. Palfray, S. Sabetay and D. Sontag. (*Compt. rend.*, 1932, 194, 1502–1505.)—The reaction $2R{\cdot}CHO+KOH\rightarrow R{\cdot}CO_2K+R{\cdot}CH_2{\cdot}OH$ does not proceed to completion when aromatic aldehydes are heated with an ethyl or butyl alcohol solution of potassium hydroxide, but it becomes quantitative when the alkali is dissolved in benzyl alcohol (b.pt. over 200° C.). The aldehyde (1 to 2 grms.) and 20 to 25 c.c. of 0·5 N solution of potassium hydroxide in benzyl alcohol are kept gently boiling for 2½ hours in a 150-c.c. conical flask of green or Jena glass (acid glass, such as Pyrex and Sibor, should be avoided), fitted with a long air-condenser tube. After addition of water, the liquid is titrated in presence of phenolphthalein to determine the residual excess of alkali. The result is corrected for that obtained in the same manner, but without the aldehyde. Benzaldehyde, anisaldehyde, tolualdehyde, cuminaldehyde and salicylaldehyde may be accurately determined by this method, which is applicable also to natural products containing aromatic aldehydes. T. H. P.

Fats of Brown Sea-weeds. B. Russell-Wells. (*Nature*, 1932, **129**, 654–655.)—In order to determine any relation between depth of immersion and the nature of the fatty constituents, four sea-weeds were examined, representing a range of habitat from a minimum covering by sea-water at spring tides in the case of *Pelvetia canaliculata libera*, to a period of being uncovered only at the same season for *Laminaria digitata*, and including the intermediate *Pelvetia canaliculata* and the slightly deeper growing *Fucus vesiculosus*. The petroleum spirit extract, and also the percentage of true fat, decreased from 8·0 and 6·2 per cent. (on the dry material) for the least immersed weed, to 0·3 and 0·16 per cent. for the most deeply immersed. The extracts were separated into unsaponifiable residue and fatty acids, and the iodine values of these, as found by the pyridine bromine method, showed no relationship similar to that of the above figures. The unsaponifiable residue, however, calculated as a percentage of the petroleum spirit extract, increased with depth of immersion. The fatty acids from the sea-weeds showing the two extremes of habitat were separated into solid and liquid portions, solid acids for *Pelvetia libera* and *Laminaria digitata* comprising 11·5, 17·7 per cent., and the liquid acids 78·7 and 72·2 per cent. The general character of the fats does not appear to be altered by depth of immersion. (Cf. *Biochem. J.*, 1929, **23**, 1000; 1931, **25**, 1472.) D. G. H.

Absorption of Oxygen by Tanning Materials. E. W. Merry. (*J. Inter. Soc. Leather Trades Chem.*, 1932, **16**, 239.)—The means used for testing the absorption of oxygen by various tanning materials, was the Barcroft differential manometer. The tanning materials tested were in the form of concentrated extracts:—quebracho, wattle, mimosa, mangrove, chestnut, and myrobalans; they are in the order of decreasing absorptive power, quebracho absorbing in 100 hours over 2 c.c. per grm. of dry matter, and myrobalans only about 0·3 c.c. The addition of sulphuric acid with and without hide powder, appeared to have little effect on the absorption of oxygen by a sample of American chestnut extract. The addition of iron alum increased the absorption power of the chestnut extract, and the addition of copper acetate increased it still more.

This is Part I of an extended research, and the results given should be regarded as preliminary. R. F. I.

Inorganic Analysis

Determination of Copper in Materials containing Rubber. F. Kirchof. (*Chem.-Ztg.*, 1932, **56**, 296.)—Direct ashing of substances containing rubber is tedious, and there is a danger of volatilisation of copper when the rubber contains sulphur chloride. The ashing process, preliminary to the determination of copper in the residue, has been improved, and the following treatment is suggested:—Ten to 20 grms. of the substance are cut into small pieces, and wetted with dilute nitric acid, an excess of sulphuric acid (10 to 20 c.c.) is added, the containing beaker is covered with a glass cover, and the whole is heated on a steam-bath for 1 hour. The material is transferred to a capacious porcelain crucible, the portion left adhering to the glass being dissolved in a few c.c. of acetone, and a few drops of concentrated ammonia are added to the crucible, the contents of which are then evaporated to dryness, heated with a small flame to decompose the nitro-compounds, and, finally, ashed by applying stronger heat. This process occupies 1½ to 2 hours. Copper is determined in the usual manner in the solution obtained by heating the ash with a mixture of sulphuric and nitric acids. S. G. C.

Determination of Tin in Irons and Steels. J. A. Scherrer. (*Bur. of Standards J. Research*, 1932, **8**, 309–320.)—Tin is stated to be present invariably in iron and steel, usually in amounts ranging from a few thousandths to a few hundredths of 1 per cent. Methods for the determination of tin involving simple solution of the steel in hydrochloric or sulphuric acid under non-oxidising conditions, and titration of the solution with iodine, give erratic results; in some cases high results are obtained, owing to the consumption of iodine by compounds formed from impurities in the steel, and in other cases the results are low for reasons which are difficult to ascertain. The author recommends preliminary separation of the tin as sulphide before the iodimetric determination, but states that precipitation of the sulphide is incomplete unless the sample is completely oxidised as described below.

METHOD I, FOR MATERIALS DECOMPOSABLE BY NITRIC ACID.—*Preparation of Solution.*—To a 10-grm. sample contained in a 600-c.c. beaker, 250 c.c. of dilute nitric acid (1:4) are added. The whole is heated until the sample is completely decomposed. An excess of saturated aqueous potassium permanganate is added, and the solution is boiled for 5 minutes, after which sufficient sulphurous acid is added to dissolve the brown manganese oxide which is formed, and the liquid is again boiled for 5 minutes. Either of the following treatments are then given: (*a*) *Treatment when tungsten is absent.*—If any undissolved matter remains, it is filtered off, and the filtrate is reserved. The filter-paper (with the residue) is placed in a 500-c.c. Erlenmeyer flask, and the organic matter is destroyed by "fuming" with 10 c.c. of sulphuric acid, with the addition of nitric acid from time to time. The residue is dissolved in water, the solution is diluted to 100 c.c., and 10 grms. of tartaric acid are added; it is then neutralised with ammonia (no indicator is specified), and added to the reserved filtrate. (*b*) *Treatment when tungsten is present.*—The liquid is kept overnight, and the clear liquid is decanted and reserved. To the residue in the beaker 20 c.c. of sulphuric acid and 30 c.c. of water are added, and the whole is heated until sulphuric acid fumes are given off; 10 c.c. of concentrated nitric acid are added, the liquid is again evaporated until fumes appear, cooled, diluted to 100 c.c., and a slight excess of ammonia is added, followed by 10 grms. of tartaric acid; the solution is then neutralised and added to the reserved filtrate.

Precipitation and Determination of the Tin.—A rapid stream of hydrogen sulphide is passed for 45 minutes into the cooled solution diluted to 550 c.c., and the precipitate is filtered off after 1 to 2 hours and washed with slightly acid ammonium sulphate solution (5 per cent.) saturated with hydrogen sulphide. The paper and precipitate are heated with sulphuric and nitric acids to destroy the organic matter, the liquid being finally heated until it fumes strongly, cooled, and diluted to 100 c.c. (Where tungsten is present, 10 grms. of tartaric acid are added, followed by a slight excess of ammonia, the solution is boiled, and cooled, and 10 c.c. of sulphuric acid are added, any precipitate being filtered off and rejected.) The solution is diluted to 550 c.c., and the tin is re-precipitated with hydrogen sulphide, the precipitate being filtered off and decomposed, together with the filter-paper, as before, and the solution is diluted to 100 c.c. Fifteen c.c. of hydrochloric acid are added, any insoluble matter being filtered off and rejected. About 40 mgrms. of iron (as chloride or sulphate) are added to the solution, which is heated to boiling, a moderate excess of ammonia is added, and the precipitate of iron and tin hydroxides is filtered off and washed with very dilute ammonia, and then with water. The precipitate is dissolved off the paper with a hot mixture of 80 c.c. of concentrated hydrochloric acid and 100 c.c. of water. The solution is diluted to 350 c.c. in a 500-c.c. Erlenmeyer flask, 10 grms. of granulated lead are added, and the flask is fitted with a rubber stopper, pierced with three holes carrying the following attachments: (1) a leading tube; (2) an air condenser consisting of a 12-inch length of glass tubing, $^9/_{16}$th inch in diameter, constricted somewhat at the end passing through the stopper, and fitted at the other end with a U-tube containing enough water to act as a trap; (3) a removable glass plug. A stream of carbon dioxide is passed through the apparatus, in which the solution is boiled gently for 30 to 40 minutes. The carbon dioxide supply is maintained while the liquid is cooled to 10° C., 5 c.c. of starch solution (1 per cent.) are then added by way of the air condenser, and the jet of a burette containing 0·01 *N* iodine solution is inserted in the third hole. The titration is carried to the first shade of blue; the volume of iodine solution used in a "blank" is deducted; 1 c.c. of 0·01 *N* iodine $\equiv$ 0·0005935 grm. of tin.

METHOD II, FOR ALLOY STEELS NOT DECOMPOSED BY NITRIC ACID.—(*a*) *In the absence of tungsten.*—A 10-grm. sample is decomposed by heating with 130 c.c. of sulphuric acid (1:5); the liquid is oxidised with 25 c.c. of nitric acid (1:1), an excess of saturated permanganate is added; the liquid is boiled for 5 minutes, and the process is continued as in Method I. (*b*) *In the presence of tungsten.*—A 10-grm. sample is decomposed as in (*a*), the liquid being filtered and the filtrate oxidised with permanganate and reserved. The residue and filter-paper are decomposed by "fuming" with sulphuric acid as in Method I (*b*). The sulphuric acid residue is diluted to 100 c.c., boiled well to ensure the soluble part being dissolved, and a slight excess of ammonia, followed by 10 grms. of tartaric acid, is added. The liquid is again rendered ammoniacal, digested on a steam-bath until solution is complete, an excess of 5 c.c. of sulphuric acid is added, and the liquid is digested on a steam-bath for half-an-hour. If solution is not then complete, the insoluble matter is filtered off, the residue and filter-paper are decomposed with sulphuric and nitric acids, and the solution is united with the other. The solution is neutralised with ammonia, added to the reserved filtrate, and the precipitations and determination of the tin are carried out as in Method I. The processes are supported by the results of numerous test experiments.

S. G. C.

Determination of Vanadium in Steel according to the Potentiometric Titration Method of Thanheiser and Dickens. P. L. Blanken. (*Chem. Weekblad,* 1932, **29**, 263–264.)—In this method (*Ber.* No. 85, *Chemikerausschusses des Vereins Eisenhüttenleute*) 1 grm. of steel is dissolved, so far as possible, in 30 c.c. of 15 per cent. sulphuric acid, and (if tungsten is present) 50 c.c. of phosphoric acid (sp.gr. 1·3). A 2·5 per cent. solution of potassium permanganate is then added until the solution is strongly red, the mixture is boiled, and ferrous sulphate is added until there is no further change in colour (which becomes green if chromium is present). The solution is then diluted with 200 c.c. of 10 per cent. sulphuric acid, and 5 c.c. of potassium permanganate solution are added in excess of that required to produce a weak rose colour. After 1 minute at 20° C. the vanadium is oxidised to the pentavalent state, the excess of permanganate being then reduced with an excess of oxalic acid. The author has now shown that if this excess is about 25 per cent., from 0·1 to 0·2 per cent. of vanadium in steel, in the presence of chromium, tungsten, molybdenum and nickel, may be determined with an error of less than 0·04 per cent. by potentiometric titration with 0·01 N ferrous sulphate solution, according to the equation $VO_4''' + 6H^{\cdot} + Fe^{\cdot\cdot} = VO^{\cdot\cdot} + Fe^{\cdot\cdot\cdot} + 3H_2O$. A platinum electrode is placed in a solution of the sample, which should be well stirred, and which is linked up with a N calomel electrode through a bridge containing a saturated solution of potassium sulphate (chlorides interfere). J. G.

Separation and Determination of Titania as Titanium Potassium Iodate. H. T. Beans and D. R. Mossman. (*J. Amer. Chem. Soc.*, 1932, **54**, 1905–1911.)—Potassium iodate produces a crystalline precipitate in acid titanium solutions; the precipitation is quantitative under the following conditions: The solution is treated with 27 c.c. of strong nitric acid, and diluted to 200 c.c. A solution of 10 grms. of potassium iodate in 100 c.c. of water and a few drops of nitric acid are slowly added to the solution during agitation. After an hour's standing with occasional stirring, the flocculent precipitate should assume a crystalline form. It is filtered off by decantation and washed five times with 20 c.c.-portions of 2 per cent. potassium iodate in nitric acid (6 per cent. by volume). Filter and precipitate are returned to the beaker and stirred up with 15 c.c. of strong hydrochloric acid. After slight dilution, sulphur dioxide is passed until the brown colour is discharged. The solution is further diluted to 300 c.c., the sulphur dioxide boiled off, and the titania determined by precipitation with ammonia as usual.

A single precipitation separates titania from alumina (0·2 grm.), lime (0·1 grm.), nickel oxide (0·4 grm.), and larger amounts of magnesia. Double precipitation removes 0·35 grm. of alumina and 0·2 of lime. Larger amounts produce adsorption. In double precipitations the solution is re-treated after removal of the sulphur dioxide by boiling as described above. The separation from phosphoric acid is effective. Manganese gives a slight dark-brown deposit; the solution of the iodate precipitate is, therefore, treated with a little ammonium bisulphite, and the titania precipitated as basic acetate. Iron is completely precipitated under the conditions described; the authors remove it by Rothe's ether extraction method (*cf.* Barnebey and Isham, ANALYST, 1910, **35**, 456). Three extractions are made, the aqueous layer is freed from ether and its acidity is adjusted by an evaporation to 50 c.c., and the titanium is precipitated as iodate. The solution of the iodate precipitate is to be treated by the basic acetate process, as in the case of manganese. Zirconium in small amounts can be precipitated as iodate from 0·3 N sulphuric acid solution, titania being kept in solution by means of hydrogen peroxide. When the filtrate from the zirconium precipitate has been freed from hydrogen peroxide by boiling, the titania is precipitated as iodate. If more than 0·01 grm. of zirconia is present, adsorption of titania by the zirconium precipitate becomes pronounced. Vanadium also interferes. W. R. S.

Determination of Free Lime in Cement. N. A. Tananaeff and L. M. Kulberg. (*Z. anal. Chem.*, 1932, 88, 179–183.)—The method is based on the reaction $HgCl_2+CaO+4KI+H_2O=CaCl_2+2KOH+K_2HgI_4$ in alcoholic solution, and titration of the dissolved alkali. The powder (0·2 to 0·5 grm.) is weighed into a conical flask with ground glass stopper; powdered mercuric chloride (about twice as much as is equivalent to the free lime), 15 glass beads, and 20 to 25 c.c. of absolute alcohol are added. The stoppered flask is shaken for 15 to 20 minutes; free lime is indicated by a yellow coloration (mercuric oxide). The liquid is filtered, the beads being retained in the flask; washing is effected with absolute alcohol until the mercuric chloride is completely removed (ammonium sulphide test). The washed powder is then treated with a hot potassium iodide solution in absolute alcohol, the yellow coloration being discharged. Washing is continued until a few drops of filtrate, added to a little phenolphthalein left after evaporation of the indicator on a watchglass, fail to produce a pink tint. The filtrate is diluted with 30 c.c. of cold water, and titrated with 0·1 *N* acid against methyl orange. The determination is carried out in 40 minutes. W. R. S.

Iodimetric Determination of Sulphur in Polysulphides. P. Szeberényi. (*Z. anal. Chem.*, 1932, 88, 187–189.)—In alkaline solution, iodine oxidises sulphur according to $S+6I+4H_2O=H_2SO_4+6HI$ (1). The reaction is utilised in the analysis of polysulphide, three aliquot portions of solution being taken. In the first, the sum of monosulphide and thiosulphate is determined:

$$Na_2S_x+2I=2NaI+S_x \ (2); \text{ and } 2Na_2S_2O_3+2I=2NaI+Na_2S_4O_6 \ (3).$$

The second portion is treated with excess of zinc or cadmium acetate solution, and the thiosulphate in the filtrate determined (3). The third portion is treated with more than enough 2 *N* alkali to yield a solution of *N* alkalinity, and an excess of 0·1 *N* iodine solution. The liquid is boiled until the turbidity caused by precipitated sulphur has disappeared; it is then cooled, acidified, and the excess iodine titrated as usual. The sulphur is oxidised as in (1), while the thiosulphate consumes eight times as much iodine as in equation (3):

$$Na_2S_2O_3+8I+10NaOH=2Na_2SO_4+8NaI+5H_2O \ (4).$$

The volume of iodine consumed in the titration of the third portion, less eight times the volume consumed in the titration of the second portion, gives the measure of the total sulphide sulphur; the total sulphide sulphur, less monosulphide sulphur (2), gives polysulphide sulphur. W. R. S.

Determination of Silica by Means of Perchloric Acid. F. W. Meier and O. Fleischmann. (*Z. anal. Chem.*, 1932, 88, 84–92.)—For the decomposition of acid-soluble silicates (Portland cement, blast furnace slag, water-glass) the following procedure is recommended: The substance is finely ground in agate, and 1 grm. weighed into a conical flask provided with a reflux condenser (ground-glass joint). It is made into a cream with 10 c.c. of water, and heated with 15 c.c. of perchloric reagent, containing 60 per cent. of perchloric acid and 7 per cent. of concentrated hydrochloric acid (sp.gr. 1·19) on a sand-bath, until white fumes are given off. The cooler is then inserted, and heating continued for 15 minutes. The hot solution is diluted with 70 c.c. of 10 per cent. hydrochloric acid, digested for 5 minutes at 90° to 100° C., and filtered hot; the precipitate is washed with hot 10 per cent. hydrochloric acid, finally with a little water, and ignited as usual. The determination requires one hour. W. R. S.

Physical Methods, Apparatus, etc.

Refractometric Determination of Organic Acids. G. Allard. (*Bull. Soc. Chim.*, **1932**, **51–52**, 372–376.)—If the volume of a 0·99 *N* solution of lead acetate, added to a solution of oxalic or malonic acid, is plotted against the refractive index (*n*) of the mixture, two straight lines are obtained corresponding with the decrease and increase in *n* with decrease in concentration of acid and increase in concentration of lead acetate, respectively, and intersecting at a point corresponding with the amount of the latter required to precipitate all the organic acid present. Optimum results, corresponding with the most acute angles between the lines, are obtained for 0·25 to 0·0025 *N* acids, and the solubility of the lead salts is sufficiently small to reduce the error, as a rule, to below 2 per cent. A suitable working-volume is 20 c.c., the reagent being added from a micro-burette so as to avoid errors due to a large change in volume. Mixtures of oxalic and malonic acids may be titrated, with errors of 0 to 3 and 6 per cent., respectively. The graph in such cases consists of 4 straight lines corresponding, in succession, with precipitation of lead oxalate, soluble lead malonate (a short portion), precipitation of lead malonate, and an excess of lead acetate, respectively. The Zeiss immersion-refractometer is recommended, and the temperature should be controlled to within 0·2° C. or the readings corrected for temperature accordingly. J. G.

Restoration of Museum Objects. A. Scott. (*J. Soc. Arts*, 1932, **80**, 488–494.)—Since the last of the three published Reports on the restoration of museum objects (ANALYST, 1927, **52**, 81) new substances have been employed, and more severe tests as to permanence have been applied. The types of deterioration dealt with include the following:

CRYSTALLISED SALT IN STONE.—To preserve stone which has been buried in moist soil containing soluble salts it is necessary to remove these salts. Soaking the object in water only results in the resulting solution of salts being immediately drawn further into the porous body of the dry stone. The most effective method is to apply to the surface of the object wet blotting-paper pulp containing only sufficient water to dissolve the salts and retain them, and then to allow the pulp to dry from the outside only. For the removal of crystallised salts from cuneiform tablets, three successive coats of celluloid solution were applied, and the tablets were then placed in relays of distilled water, with the result that the salt was dissolved and diffused into the outside water.

GREASE STAINS.—These may often be removed by means of pyridine.

REMOVAL OF "FOXED" MARKS.—The brown stains produced by the growth of mould fungi can be removed by treatment with a 2 per cent. solution of chloramine-T, without affecting any of the ordinary pigments used in water colours. Pictures thus treated have been exposed to strong daylight for five years without any change of the tints being detected.

"BRONZE DISEASE" OF COPPER.—The deterioration of the surface of copper objects which have been buried in the soil is known as the "bronze disease"; it is due to the action of chlorine, generally derived from sodium chloride in the soil. The best method of preserving the patina, consisting of hard stannic oxide coloured by copper compounds, is to soak the object in sodium sesquicarbonate solution. This gradually removes the chlorine without attacking the patina, and the object is then thoroughly washed with water. In more aggravated cases it may be necessary to strip off all compounds, *e.g.* by soaking in a 3 per cent. solution of citric acid, or even to treat the object "electrolytically" with zinc and sulphuric acid or caustic soda solution.

TREATMENT OF FRIABLE LEATHER.—A brittle roll of Ancient Egyptian leather was rendered flexible by coating it with three coats of a 2·5 per cent. solution of celluloid in such a way that the various folds did not adhere together, and, when it was thoroughly dry, applying a 5 per cent. solution of celluloid. It could then be unrolled and pressed flat under a sheet of glass.

FOURTEENTH CENTURY GLASS OF WELLS CATHEDRAL.—A peculiar coating on the windows in the Lady Chapel of Wells Cathedral was found to consist of calcium sulphate in small nodules. The sulphuric acid had originated from the combustion of the gas used for lighting the cathedral, which had condensed on the windows, where it had combined with the fine powder derived from the soft limestone with which the floor was paved.

REMOVAL OF TAR FROM MARBLE.—A white marble bust which had been exposed to the smoke from a fire was covered all over with black tarry particles. To prevent the solution of the tar in a solvent from sinking into the marble, it was necessary to use an emulsion of benzene, dilute aqueous ammonia solution, and methylated spirit. When this was applied with a tuft of cotton wool, the drops of benzene picked up the particles of tar, whilst the water, assisted by the methylated spirit, penetrated the uncovered marble, thus keeping out the benzene solution of tar. On then wiping the surface the bust was left as white as it was originally.

MARBLE STAINED WITH RED INK.—Every trace of the red colour was removed by means of chloramine-T without roughening or injuring the polished marble surface of a bust.

Reviews

ANNUAL REPORTS ON THE PROGRESS OF APPLIED CHEMISTRY FOR THE YEAR 1931. Vol. XVI. Published by The Society of Chemical Industry. Price, members 7s. 6d.; non-members 12s. 6d.

Everyone interested in the chemical aspect of industry awaits with impatience the Annual Reports issued by the Society of Chemical Industry. All concerned are to be congratulated on the early publication this year and on the general high standard of the various articles of which the volume consists. These articles or sections are twenty-four in number, and cover effectively the whole range of chemical activity from fuels to food, from soils to sanitation, from gas to glass, from metals to medicinal substances, and each review of the year's work in one particular section is written by a specialist in that branch. Naturally it does not always follow that the specialists as such are capable of presenting to the waiting world of chemists a balanced record of the progress of the last twelve months. In fact, as specialists, they may be biassed to one way of thinking, and therefore may not give due prominence to suggestive work at variance with their own particular views. It is a difficult task to present a short synopsis of the vast amount of work which appears during any one year, and the method of presentation varies. At one end of the scale is the descriptive article, with a more or less serious attempt to sift the grain from the husk; at the other end the index type, where the reviewer is content to give a whole list of references with little criticism or discernment. Both methods have their advantages, and, as would be expected, the articles published in the volume under review are generally a blend with a bias towards one type or the other. Whether we agree with the method pursued or not, it can certainly be said that the volume, running to over 600 pages (with efficient name and subject indexes of more than 50 pages), is an invaluable one, and should certainly be in the hands of every chemist, not only the industrial chemist, but also the so-called "pure" chemist, for the boundary between them becomes progressively thinner and less distinct.

L. H. LAMPITT.

APPLIED CHEMISTRY. By C. K. TINKLER, D.Sc., F.I.C., and HELEN MASTERS, B.Sc. Vol. II (Foods). Second Edition. Pp. 284. London: Crosby, Lockwood & Son. Price 15s.

This is the second edition of the volume, which was published first in 1925. The changes are slight, but important; they comprise adequate references to the regulations with regard to preservatives, some references to recent analytical work, and some slight modifications which were suggested in reviews of the first volume.

In reviewing this book the writer feels that he cannot express his opinion better than by the following abstract from his original review:

"This volume is written for students of household science and public health. It is described in the preface as dealing with 'certain branches of the chemistry of food and with the interpretation of the analytical results obtained,' but its scope is not so limited as this description might suggest, as is shown by the following list of contents:—Milk, 31 pages; Edible Oils and Fats, 33 pages; Carbohydrate Foods, 63 pages; Raising Agents, 29 pages; Meat, Meat Extracts, etc., 19 pages; Vinegar, Fruit Juices and Vegetable Acids, 17 pages; Beverages, 13 pages; Preservation of Food, Condiments, etc., 36 pages; The Calorific Value of Foods, 12 pages.

"There can be no doubt that the book adequately fulfils its purpose, for it is obvious throughout that the authors have desired not only to present the necessary information, but also to ensure a thorough understanding of the chemical principles involved. This latter is such a feature of the book that, although it is written expressly for a special university course, it might well be read with profit by students who need a fuller knowledge of the chemistry of food. Excellent examples of the educational value of the book are the explanation of the iodine value of an oil or fat, pages 42 to 46; Chapter IV, on Raising Agents; Chapter VI, on Vinegar, etc.

"The analytical methods given are those usually employed in routine analysis, and are well described. The necessary calculations are particularly carefully explained, though the extreme attention to detail in some of these suggests rather poor arithmetical ability on the part of the students.

"Cocoa and Chocolate, pages 200 and 201, receive meagre treatment, and no analytical work is described.

"A description of a method of determining the amount of stalk in tea might have been included as being of use to students of household science; also, a method for estimation of chicory in coffee mixtures might have been given.

"The volume bears evidence throughout of careful and considered compilation, and is of real educational value."

E. B. HUGHES.

AN INTRODUCTION TO BIOCHEMISTRY. By ROGER J. WILLIAMS, Ph.D. Pp. xiv+501. London: Chapman & Hall, Ltd. 1932. Price 21s.

The idea which inspired the writing of this book is a good one—namely, that a knowledge of biochemistry is to-day essential for all students of chemistry, and that a course in the subject should, therefore, find a place in every chemical curriculum. The difficulties of drawing up a well-balanced outline of biochemistry are, however, great, and it cannot be claimed that Professor Williams has succeeded in dealing with them. Success in presenting a wide view of a subject depends on the ruthless removal of confusing detail, and in several sections of this book the pruning knife has not been applied with sufficient vigour.

The book is divided into sections dealing with the composition of organisms, their nutritional requirements, the mechanisms used by them for promoting and regulating chemical change, and three sections on metabolism. The latter are undoubtedly the best part of the book, and are worth attention. There is also an addendum on suggested laboratory experiments, which the author probably finds useful to his own classes, but which will not supersede the recognised standard text-books on this side of the subject, and which appears to be a little out of place. Though much detailed biochemical information is offered, few references are given. The book, therefore, cannot be used as a work of reference by the trained chemist. It appears more than likely that the chemist in training will find parts of it very confusing, and, moreover, will form the erroneous impression that biochemical research is carried out almost exclusively in North America.

The printing is good, but the price is excessive.

DOROTHY JORDAN LLOYD.

THE GLYCOSIDES. By E. F. ARMSTRONG, D.Sc., Ph.D., LL.D., F.R.S., and K. F. ARMSTRONG, B.A., B.Sc. Pp. vii+123. London: Longmans, Green & Co. 1931. 12s. 6d.

The section on glucosides in the Simple Carbohydrates and the Glucosides has now been re-written and brought up-to-date, and appears as a separate volume in the well-known series of monographs on biochemistry. The term "glycoside" is stated to be the new official name for the large number of substances containing sugars linked to one or more other compounds: "glucoside" is now the specific name used for those glycosides, the sugar constituent of which is glucose. The non-sugar parts of the glycosides are referred to as "aglucones," a term originating with the Japanese chemists. The complex and diverse nature of the aglucones is illustrated by the headings of the chapters: Natural Glycosides (Phenols, Hydroxyanthraquinones and Hydroxycoumarins); Glycosides of the Soluble Plant Pigments (Anthoxanthins and Anthocyanins); Glycosides with Physiological Action (Digitalis, Strophanthin, Saponin); Other Natural Glycosides (Mustard Oils, Cyanophoric Glycosides, Nucleosides, Indican, Pentosides); Synthetic Glucosides; Uronic Acids.

The functions of glycosides in plants are discussed, and it is pointed out that no one explanation will cover the activities of all the members of the group. According to the authors, aglucones in the free state oxidise, polymerise and undergo other changes, but are stable when linked to sugar molecules. They thus remain dormant until liberated by the appropriate enzyme, when they become the hormones or activators of plant cells. In an interesting discussion on glycosides and animal nutrition, it is suggested that this stimulating action of the constituents of glycosides also determines, to some extent, the nutritive value of herbage. The non-sugar constituents can frequently be detected with certainty, and also estimated quantitatively, and glycosides are, therefore, likely to become of importance analytically.

The final chapter is devoted to the utilisation of carbohydrates in plants, the main points reviewed being the protection afforded to the plant against low temperatures by the presence of carbohydrates, and the changes in the nature and amounts of carbohydrates during the growth, ripening and storage of fruits.

To all those concerned with plants and plant materials this concise monograph, with its extensive bibliography, will be invaluable. H. PHILLIPS.

RECENT APPLICATIONS OF ABSORPTION SPECTROPHOTOMETRY. Compiled by the Advisers and Staff of A. Hilger, Ltd. Pp. 44. London: A. Hilger, Ltd. 1932.

This small volume is intended to serve as a supplement to *The Practice of Absorption Spectrophotometry with Hilger Instruments*, and consists of a bibliography of the principal papers published in this country, in America and on the Continent during the last ten years.

It is divided into four parts, each of which is sub-divided according to the portion of the spectrum employed, the subject treated of, or the title of the publication in which the paper appeared.

Part I, by Dr. W. R. Brode, gives the titles and a brief summary of 137 papers on physics, physical, inorganic, organic, and biological chemistry and industrial colour measurement, published between 1922 and 1927. Part II provides a similar selection of 211 papers (excluding those on biochemistry, which have been relegated to Part IV) appearing between 1927 and 1931. Part III, by Dr. S. Judd Lewis, comprises a supplementary list of publications in the *Berichte*, *Biochemische Zeitschrift*, *Biochemical Journal*, and the *Proceedings of the Royal Society*; while Part IV is devoted mainly to papers on biochemistry and pathology, over half of these dealing with the important subject of vitamins and allied substances. The publishers have shown commendable enterprise in the publication of such a well-produced monograph, which will be widely welcomed by workers in many branches of science, by whom the utility of such a compilation will be greatly appreciated.

T. J. WARD.

INDUSTRIAL CHEMICAL CALCULATIONS. By O. A. HOUGEN, Ph.D., and K. M. WATSON, Ph.D. Pp. 502. London: Chapman & Hall, Ltd. **1931.** Price 28s. 6d.

This book is concerned mainly with the indefinable borderland between applied physical chemistry and engineering, and should, therefore, appeal both to engineers interested in chemistry and to chemists whose work brings them into contact with engineering problems. In addition, it should prove very useful to the student of chemical engineering, although the fully-qualified chemical engineer will probably find it rather elementary.

The authors start from fundamental principles, such as the compounding of mixtures and stoichiometry. This leads to a consideration of the kinetic theory, to which considerable attention is devoted, in spite of its limitations. The authors recognise the existence of these limitations (although, unfortunately, they do not state them), but believe, rightly, that the theory provides a clear-cut mental picture of the mechanism of changes in energy and lends itself to simple mathematical treatment. Gaseous mixtures, vaporisation, crystallisation and adsorption are then considered, and, except for short chapters on distillation and chemical equilibria, the remainder of the book is devoted to thermo-physics and thermochemistry (including weight- and heat-balances and fuels). The section on coal should be of particular interest to the analyst.

In each chapter the procedure is to outline, in simple terms, the fundamental physico-chemical theory, and then to demonstrate its mathematical treatment. Worked examples and numerous problems applying to a great variety of industries illustrate the principal points. The authors have spared no pains to clarify their mathematical working by labelling each individual step, and, if this has added considerably to the length of the book, it has the advantage that the non-mathematical reader need not be frightened by the title. Arithmetical short-cuts have been purposely avoided, and even if the desirability of such a policy is admitted, there is, in the reviewer's opinion, no excuse for the omission of a chapter on other aids to rapid calculation. It is surprising, for example, how many chemists are strangers to the slide-rule, and no chemical engineer can be said to have completed his education without a knowledge of nomography. A few pages on nomogram-construction, illustrated by some typical examples, would have added considerably to the value of the book.

Apart from this, there is little other than praise for the book. It is written in a style which will appeal to English readers, and it is well-produced. The mathematics are sound, and those problems tested did not give impossible results. The use of B.T.U. (instead of B.Th.U.) for the British Thermal Unit does not distinguish it from the Board of Trade Unit, but this is one of few misprints, and is, possibly, excusable in a book of American origin.

JULIUS GRANT.

SOAP. By W. H. SIMMONS, B.Sc. (Lond.), F.I.C. Pp. ix+134. London: Sir Isaac Pitman & Sons, Ltd. Price 3s.

This little volume, which has recently appeared in the form of a third edition, gives a succinct and very readable account of the various features connected with soap manufacture and glycerine recovery. Writing for those not necessarily familiar with chemistry, Mr. Simmons has succeeded in the very difficult task of reconciling scientific accuracy and clarity with the use of perfectly simple English, and has done this without evading many specific terms, both chemical and technological, which are pertinent to the subject. He introduces technical phraseology in such a manner that one feels that the reader must subconsciously realise not only its meaning, but its *utility*. This last-mentioned virtue seems frequently to be overlooked by those well-meaning individuals who love to rate chemists for writing in a "language" which the uneducated cannot understand; admittedly there are two extremes in the matter, but Mr. Simmons shows that both can be avoided.

The technical descriptions are clear and cover practically the whole of the art of soap-making; of course, the treatment cannot be exhaustive within a matter of 130 small pages, but it is remarkable how much has been collected together in this limited space. One believes that the book will be useful, for example, to many readers of this journal who wish to acquire a rapid acquaintance with the conditions of manufacture of different types of cleansing material. Most attention is devoted to household, toilet, shaving, soft and textile soaps; soap powders, dry soaps, etc., are briefly dealt with, and possibly might, with advantage, have received a little more space. Similarly, distilled glycerine is rather briefly handled by comparison with the evaporation processes for the production of crude glycerines, which are very well explained.

In one or two minor points the author's views are, perhaps, open to question. Thus the hydrogenation processes are said (p. 7) to lead to a "depletion of the soap-makers' resources" by diversion of soap-making raw materials into fats of edible quality; but surely, on balance, the soap-producer has gained as much, or more than, the edible-fat manufacturer, since a number of oils, especially whale oil, which were formerly useless, or only usable as "soft" oils, have by this means been converted into potential sources of fats of the hardness of tallow. From p. 26 it might be concluded that alkaline silicates are made by concentration of neutral silicate solutions to 140° Tw., and it would possibly have been better to make it clear that the composition of the two grades is controlled by the proportions of soda-ash and sand in the original melt. The present book probably retains traces of earlier editions when it is suggested, here and there, that glycerine is the most valuable product of the soap factory; certainly this was true ten or fifteen years ago, but times have changed since then!

The short section on "commercial valuation of soap" (pp. 106–107) is of especial interest to the analyst. It may be doubted whether Mr. Simmons's desire for a "legal definition of what is soap" would prove to be in the best interests of the consumer; so many classes of soap, different in cost but with definite uses, are on the market that, as indeed he points out, account must be taken of a number of factors in considering the specification for any given soap. T. P. HILDITCH.

AUGUST, 1932 Vol. LVII., No. 677

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

NORTH OF ENGLAND SECTION

THE Third Summer Meeting was held at the Queen's Hotel, Scarborough, from July 1st to 4th. The attendance numbered sixty-one, including many ladies.

Among those present were the following:—Past Presidents (Mr. A. Chaston Chapman accompanied by Mrs. Chaston Chapman, Mr. E. R. Bolton, Dr. Dunn with Mrs. Dunn); Hon. Secretary (Dr. G. Roche Lynch); Hon. Treasurer (Mr. E. B. Hughes with Mrs. Hughes); Editor of THE ANALYST (Dr. C. A. Mitchell); Mr. E. M. Hawkins; and Miss Elliott.

On Saturday afternoon Mr. E. R. Bolton read a paper on "The Edible Fat Industry, with Special Reference to Hydrogenation." A telegram was sent to the President (Mr. F. W. F. Arnaud) expressing the regret of the members that he was unavoidably absent. A resolution of congratulation was passed unanimously to Dr. W. R. Schoeller on his receipt of a Beilby Memorial Award mainly for work done under the Analytical Investigation Scheme.

The Chairman (Mr. John Evans) extended a cordial welcome to all attending the meeting, especially those from the south. He also proposed a resolution, which was passed unanimously, conveying the greetings of the Section, and expressing its goodwill and loyalty to the Council.

Various forms of recreation were enjoyed, and Dr. Dunn rendered pieces of music from old English masters. On Sunday afternoon the party proceeded by motor through Whitby to Sandsend Hotel, where tea was taken. Perfect weather conditions prevailed throughout the meeting.

A clever cartoon, entitled "A Few Ancient Analysts," was specially drawn by Mr. G. L. Wollaston for the menu of the dinner on July 2nd.*

A vote of thanks to the Hon. Secretary of the Section (Mr. J. R. Stubbs) was proposed by the Chairman, and passed unanimously.

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* Copies of this cartoon can be obtained, free of charge, on application to the Honarary Secretary of the North of England Section (Mr. J. R. Stubbs).

Obituary

CECIL HOWARD CRIBB

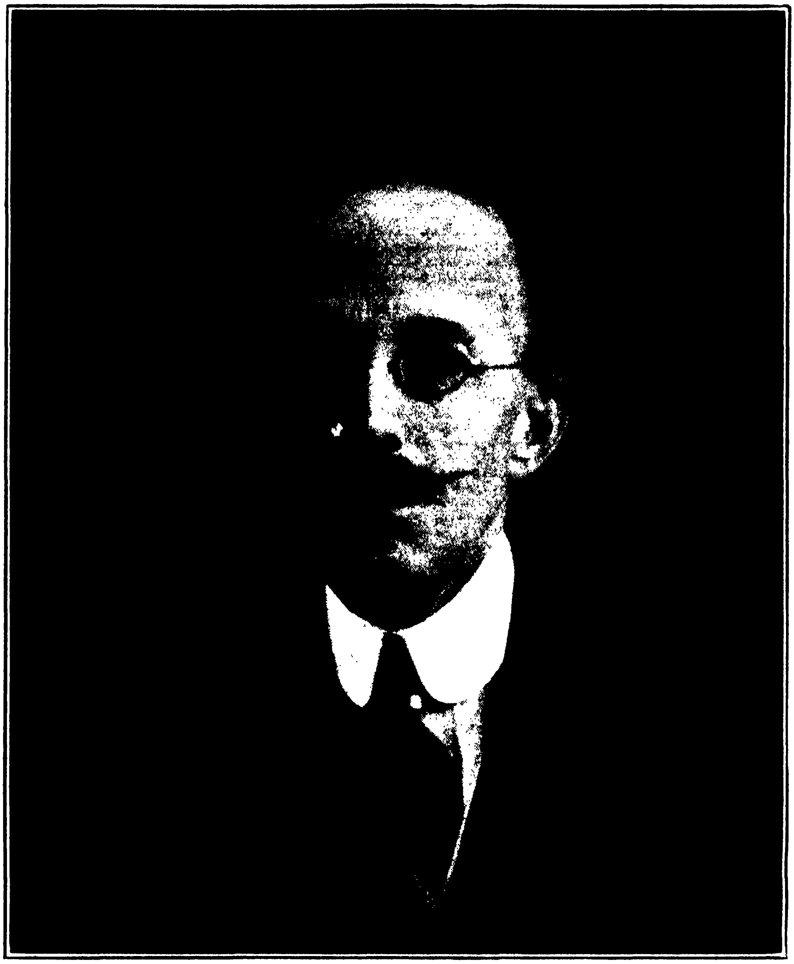
The announcement of the death of Cecil H. Cribb in the July issue of The Analyst must have been read by his many friends with great regret. On June 11th Cribb was taken seriously ill and, despite an operation, he passed away on the 13th. He was 68 years of age. By his death the Society loses one of its most ardent supporters, for, after his election as a Member in January, 1890, Cribb took a very deep interest in the affairs of the Society. From 1895 onwards he served, on different occasions, as a Member of Council, and also for two periods as a Vice-President. Since 1908 he served on the Publication Committee of The Analyst, the interests of our journal being dear to him, and up to the last month he read the proofs with unfailing assiduity and attended the prolonged meetings of the Committee with unflagging zeal. He was also greatly interested in the work of the Institute of Chemistry, and was the first Examiner (1907–1911) in the Chemistry of Foods and Drugs under the scheme of examinations introduced during the Presidency of Professor P. F. Frankland.

He received his early education at a boarding school at Leatherhead and at University College School, and about 1878 proceeded to the School of Mines, South Kensington, where he studied under T. H. Huxley and Sir Edward Frankland, among others. For nearly two years he acted as assistant to Professor Purdie, at St. Andrews University, where his manipulative skill and ingenuity proved valuable in devising lecture experiments. Afterwards he became assistant to Professor P. F. Frankland. In 1887 he registered as a medical student at University College Hospital, and covered a large part of a medical course, though he never qualified.

In the early eighties he opened a laboratory in London, and commenced practice as an analytical chemist, and this practice he carried on until his death. His first public appointment was that of Public Analyst to the Strand Board of Works (1886), and in those early days, if the food samples submitted were few in number, they provided a very considerable amount of work, owing to widespread adulteration. When the Strand became incorporated in the City of Westminster, Cribb became a joint Public Analyst for that City. The other important public appointment which he held was that of Public Analyst for the Metropolitan Borough of Fulham. During the nineties he took part, in collaboration with H. H. F. Hyndman, in experiments on the then recently discovered *X*-rays. His private practice was considerable in extent, and included the examination of a number of waters, for he was consulting analyst to several Water Companies.

The late hour to which he stayed in his laboratory every evening is a proof of his zeal for work, and those who had the privilege of working with him can testify to his ability and to his versatile brain. He revelled in attacking a difficult problem, and many days, or even weeks, would pass before his ingenious mind would exhaust phases of work which might yield the desired result.

Cribb will long be remembered for his resourcefulness in introducing new forms of chemical apparatus. Probably he is best known as the inventor of the double-surface condenser. It might well be said that until Cribb attacked the



Cecil H. Britt

methods used for the condensation of vapours in the laboratory, the Liebig condenser or a worm condenser were accepted as irreplaceable pieces of apparatus. Condensers a foot or a yard in length were reverenced, and few people had even thought that any other form of condenser was possible or permissible in a laboratory. Cribb really showed that a 4-inch upright condenser could work as efficiently as many feet of glass tubing surrounded with water. Commercially he met with a similar difficulty, that of convincing anyone that there was any apparatus that could work as efficiently as the old type of condenser. His carbon dioxide apparatus is familiar to many. This apparatus and his specific gravity bottle have features which should have made them even more popular than they have become. However, his ingenuity was by no means restricted to devising apparatus for use in the laboratory, for many other conceptions were the subject of patents taken out by him. During the cycle craze, about 1897, he invented a bicycle head which by easy treatment could be made to lock the steering of a cycle This device was actually purchased by a cycle company. Then an automatic machine for the delivery of postage stamps received his attention, but the device was in advance of public opinion, or possiblv requirements.

In 1900, Cribb published a paper on "The Influence of Temperature and Pressure on the Saline Constituents of Boiler Water." This paper showed the decomposition of various salts which occurs when waters are concentrated under pressure, etc.

Papers then followed describing the new forms of carbonic acid apparatus, and also the double-surface condenser mentioned above.

In 1905, the results of an investigation, carried out in conjunction with another investigator, were published, showing the action of slightly alkaline waters on iron. Papers written in conjunction with others were published later: on "A Method for the Approximate Determination of Boric Acid," "Analyses of Cream Cheese," "The Facing of Rice," "The Analysis of Margarine," and, a very important contribution at that date, "The Composition and Analysis of Chocolate."

He was joint author with H. Mansfield Robinson of the book "Law and Chemistry of Foods and Drugs."

Cribb was an enthusiastic collector of antiques, and of old prints chiefly relative to chemistry, and he acquired a very considerable knowledge of these. His collection of prints of the alchemists and their laboratories was very large and representative, and he also possessed many pieces of old scientific apparatus.

His recreations included cycling, lawn tennis and gardening. Though never of robust constitution, he spared himself no physical effort; in fact, he had a great belief in exercise, and for many years he cycled between his old home at East Finchley and his laboratory in the West End of London. Only the recent crowded state of the thoroughfares, and his health, made him forsake his cycle for the train. He was devoted to dogs, having a predilection for the largest breeds.

A man of broad outlook, a deep thinker, a scientist with a gift of easy conversation—how all who knew him must miss him! The sadness of his old friends at his graveside was a token of the deep affection of his fellow men for him, and the presence of so many was an appreciation of the services he so unstintingly rendered to the profession. F. W. F. ARNAUD

Castor Seed in Feeding Stuffs

BY F. ROBERTSON DODD, F.I.C.

(*Extract from a paper read at the Meeting of the North of England Section, February* 13, 1932)

OPINIONS are divided as to the desirability of stating definitely the quantity of castor which may be present in a feeding stuff, or of fixing any limit which must not be exceeded. Dr. Voelcker, Chemist to the Royal Agricultural Society, regards the giving of percentage figures for castor seed present as being utterly misleading, owing to the uneven distribution of the castor. He accordingly declines altogether to certify to percentages present, but condemns a food as unfit for use if he finds castor in it. Force of circumstances, however, compels most of us who handle the raw materials as they enter the country to state the percentages, since the new contracts specify limits.

For the County Analyst, who receives a much smaller sample than we at the ports of entry, any trace of castor seed should be sufficient to condemn the parcel, and there should be no need for him to state quantities.

When the controversy arose some years ago, my late partner suggested to the trade that a limit of 0·005 per cent. of castor seed should be fixed, but Liverpool merchants regarded this limit as too risky, and agreed to insert in the contract a clause to the effect that, if any one of three analysts found any trace of castor seed, the buyer could reject the parcel.

An unwritten opinion is current that any quantity of castor seed over 0·01 per cent. may prove fatal to cattle. This, so far as I know, is without foundation, beyond the fact that castor poisoning has occurred when no analyst has found more than 0·02 per cent. Owing to rumours which circulate in the business world, the question is now being asked whether there is a difference in the toxicity of various species of castor seed. This rumour is persistent, and does not lack the support of certain chemists. "Some castor seeds may be harmless," says the rumour, "whilst others may be deadly." To my mind there is only one course open to the County Analyst, namely, to regard all castor seeds as deadly, and to report accordingly.

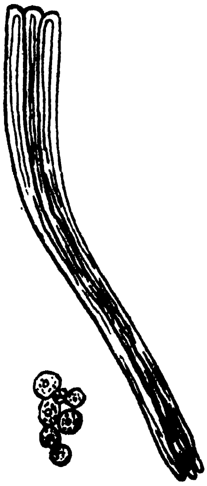
While the general details of the method for the detection of castor seeds are, doubtless, familiar to most, there may yet be some points, gathered by me in a lengthy experience, which may be found useful.

My own laboratory generally receives a sample of 7 to 10 lbs. in weight. This is broken into small pieces and quartered down, the quartered portion being passed through a mill, which reduces it to pass a sieve with ten meshes to the inch. This ground portion is passed through a Clarkson sampling machine, and the portion delivered is weighed and used for one test. The process is repeated on the portion of the original sample first broken down, until four samples of 50 to 120 grms. have been obtained.

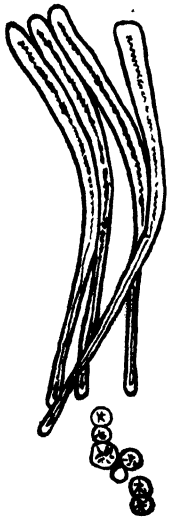
In doubtful cases further portions are prepared and treated. Certain analysts weigh 1 lb. of the sample and use that for their test, but I prefer to prepare a number of samples in the way described, the total quantity being generally between 250 and 500 grms.

The portions selected are treated with 500 c.c. of dilute sulphuric acid (1·25 per cent.), and, then after being washed by decantation, with 300 c.c. dilute sodium hydroxide solution (1·25 per cent.). The washing after the treatment with sodium hydroxide may be very important. In such materials as kapok seed cake, for example, the colouring matter is very difficult to remove and interferes with subsequent bleaching.

A solution of calcium hypochloride, sufficient to bring the liquor, in which the fibres are suspended, to a strength of approximately 1 per cent. of "available" chloride, is added and the mixture stirred frequently during the bleaching process.



Castor



Croton

For linseed cakes, the fibres of which are easily bleached, half the above strength of hypochlorite suffices. Last year certain "Russian" linseed cake contained a rather high percentage of castor seed, which bleached readily under ordinary conditions. Whether this was immature seed or not I cannot say; I merely record my experience.

As a rule, the bleaching process should not occupy more than an hour. At the end of that time the sample is washed by decantation and spread out on a white dish, and the black particles are picked out and examined under the microscope. Finally, the residue is washed quickly with dilute hydrochloric acid to remove the last traces of hypochlorite, and then with water, and again picked over, to recover any pieces of husk which have escaped the former search.

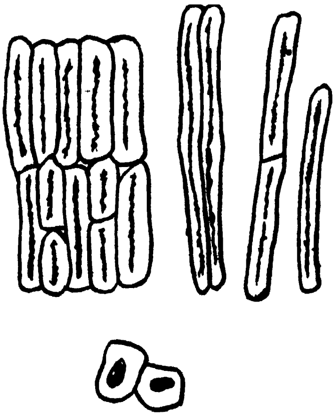
Certain foreign makers have lately been grinding seed much more finely than formerly for the extraction of the oil, and the castor-seed husk is so comminuted that it may occur in very minute particles, which are difficult to see and separate.

Identification under the microscope is, at present, the subject of adverse criticism by shippers, who accuse English chemists of incompetence, and several of us have had letters stating that we have mistaken mustard or hemp seeds for castor.

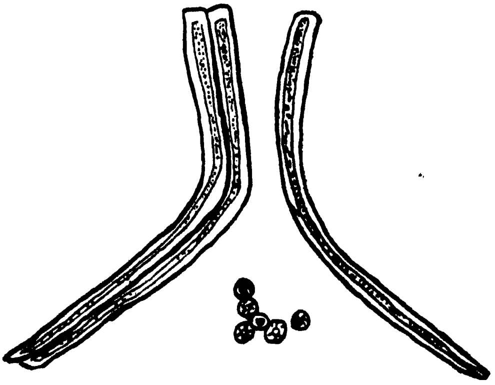
The seeds which might easily be mistaken for castor include grape or raisin seed and ucuhuba seed (possibly), both of which are harmless; croton seed and curcas seed, both more poisonous than castor.

It is usual to return castor, croton or curcas as castor seed. Ucuhuba seed presents little difficulty, but grape seed often presents a real difficulty.

Often one finds on the inner side of grape-seed husk a membrane, not unlike a finger print, which is never found on castor-seed husk, but more often there is little except the size of the "pin holes" to distinguish the two. I am referring to the blackened grape seed from wine-making processes, not to the light seeds, which bleach well.



Grape



Curcas
Palisade cells and upper surface view

The black grape husks picked out, when treated with sulphurous acid, turn purple fairly quickly, whilst the castor husks remain black for a long time.

If the husks be treated with 50 c.c. of $N/2$ hydrochloric acid and 4 grms. of potassium chlorate on a water-oven for about an hour, the palisade cells separate, and can be examined under a $\frac{1}{8}$ in. objective, when there need remain no doubt in the mind of the observer.

The diagrams, drawn with the aid of a camera lucida by a former assistant, Mr. O. A. Morch, slightly exaggerate the points to be looked for. The photographs taken by my assistants, Messrs. Telford and Waters, explain themselves. The magnifications are approximately 40 and 140. As a closing note, I may add that, when stating percentages, the system adopted in Germany is now generally required, *i.e.* the London contracts have copied the German rule of stating the percentage of castor-seed *husk* found.

The chemical treatment to which a meal is subjected before picking out the husks, extracts from castor-seed husk substances amounting to one-fifth of its weight, *i.e.* 80 per cent. only is found.

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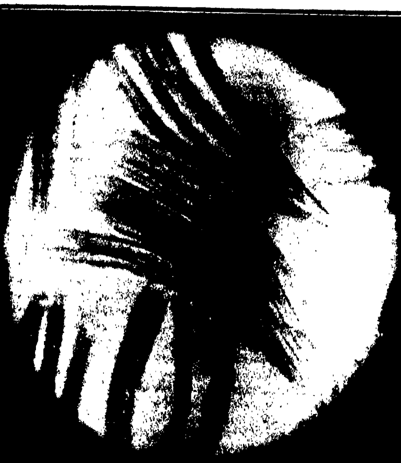

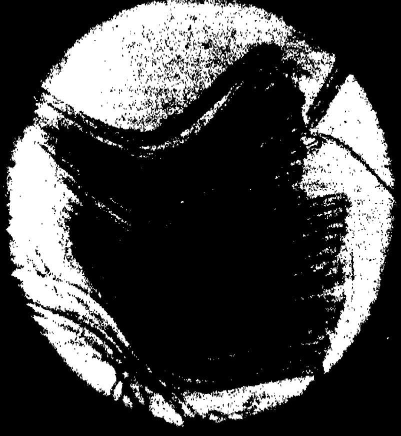

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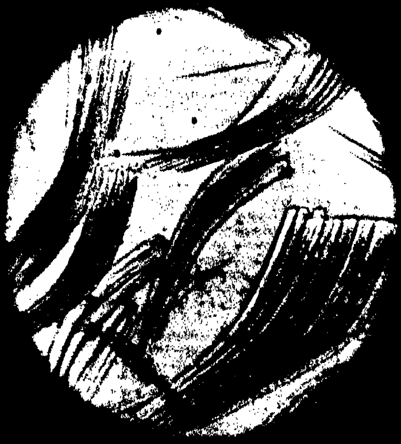

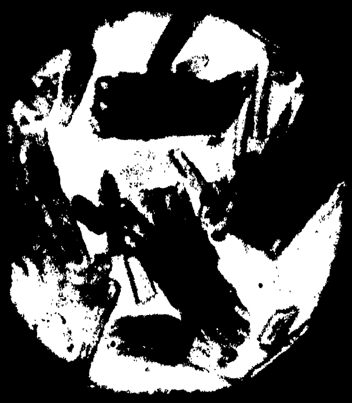

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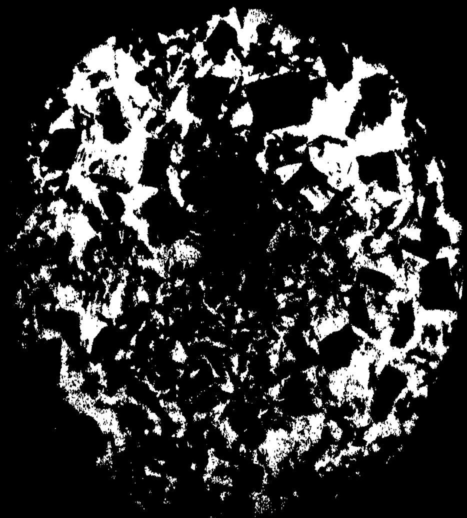

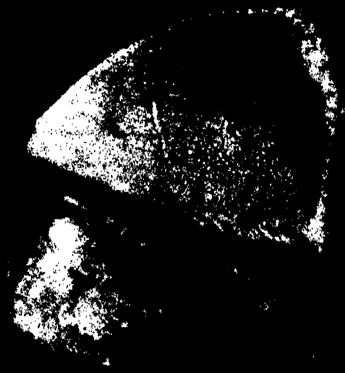

The custom, based on the average fibre content of castor seeds, is to weigh the husk found and multiply this weight by 5 to express the percentage of seed.

The weight of the husk increased by one-fourth should represent the castor-seed *husk* originally present.

An alternative method is to multiply the weight of the husk by 5 (= castor seed), and to divide this result by 4 (= castor-seed husk originally present).

(See also J. W. Leather, ANALYST, 1892, **17**, 121; Lander and Geake, *id.*, 1914, **39**, 292; Brioux and Guerbet, *id.*, 1921, **46**, 100; H. Waites, *id.*, 1922, **47**, 306; Report of Case, *id.*, 1932, 381.)

DISCUSSION

The PRESIDENT welcomed Mr. E. E. Billington, not only as a member of the Society, but also as a manufacturer who could present the manufacturers' view to the meeting.

Mr. BILLINGTON joined issue with Mr. Dodd on the statement that analysts should condemn feeding stuffs if they contained a minute trace of castor seed. He had experimented in the feeding of cattle with cakes containing 0·001 per cent. of castor seed without ill effects. He gave details of several cases of castor-seed poisoning which had been investigated, and contended that the analyst was not merely a detective and judge combined, but one to whom the community looked to investigate such subjects and to suggest measures to counteract the effects of the poison. The introduction of small quantities of castor seed into feeding stuffs was never intentional and, so far as chemical control on arrival at Liverpool and in reputable works was concerned, every attempt was made to prevent its inclusion. Other feeding stuffs could be substituted for pea nut (arachis) meal, but these would affect the fat of the milk, and particularly the character of the butter made therefrom, and manufacturers, wishful to do their best for their customers, were compelled, by monetary considerations, to use the best available materials. In spite of the most rigorous control, traces of castor seed occasionally found their way into the products, and, in cases where the total quantity present was very minute, he thought that the analyst should be merciful in his report. With regard to the acceptance by continental importers of parcels which this country had rejected, there was another reason than that given by Mr. Dodd. By the time the chemist's report was issued, showing that castor seed was present, the consignment was in barges many miles away, and the expense of bringing it back and re-delivering it to the sellers would be so great that buyers accepted delivery, *but* demanded an allowance.

Professor W. H. ROBERTS drew attention to the fact that cattle could be immunised to castor seed.

Mr. J. HANLEY confirmed this, and mentioned the different reactions of various animals to the poison. Some of his experiments (made under licence) had shown that, whilst one animal died from consuming a mixture containing castor seed, others not only showed no ill effects, but throve on the mixture. The difficulty was that when a number of animals were fed on beans and one of the animals promptly died, one could not decide whether it was a case of poisoning or of idiosyncrasy of the animal. He instanced also a case of human idiosyncrasy of an assistant who, within half-an-hour of chewing beans of unknown origin (which he did not swallow) developed a red rash all over his body. The rash did not disappear for a few days.

Mr. S. E. MELLING asked whether, in view of its well-known de-toxicating properties, active carbon had ever been tried on animals suffering from the poison; if not, he suggested that such treatment was worthy of consideration.

Mr. A. R. Tankard mentioned that, during the war, investigations made in Hull on behalf of the Ministry of Agriculture and Fisheries, had shown that it was possible to treat castor seed in such a way as to render the meal quite innocuous to live stock. He asked whether it was possible to apply any simple method to distinguish such treated meal from the actively poisonous material.

A general discussion followed, in which questions as to the action of the lipase or enzyme; the occurrence of castor seed in various materials; the effect on workers with castor seeds, etc., were mooted.

Messrs. Dodd and Billington received the thanks of the meeting for their valuable contributions to the discussion.

An Improved Method of Titrating Arsenic Precipitated by Hypophosphorous Acid*

By B. S. EVANS, M.C., Ph.D., F.I.C.

This paper is to be taken as supplementary to one published in 1929 (Evans: "A Method for the Separation and Determination of Arsenic," Analyst, 1929, **54**, 523), in which directions are given for the precipitation of arsenic by hypophosphorous acid, and its subsequent determination by solution in a measured excess of standard iodine solution and titration of the excess of iodine with arsenious acid. It was shown in that paper that with the filters then in use the "blank" could be eliminated by titrating away the iodine with a small excess of the arsenious solution and then titrating the excess of arsenic again with standard iodine (*ibid.*, p. 523). When the method was carried out in this way no appreciable "blank" was found. This method was in use, with excellent results, until recently, when an unforeseen difficulty made itself manifest. It will be noted that the principle of the method of titration was the entire removal, by an excess of arsenious acid, of the iodine absorbed on the filter pulp and giving rise to the blank; it was now found that, owing, presumably, to a change in the manufacture of the filter paper, the intense blue colour of the latter in presence of iodine could not be removed with any reasonable excess of arsenious solution. As this "blueing" of the pulp made it practically impossible to get an end-point by the original method, I attempted to substitute benzene for the starch in the preliminary titration, only adding starch for the final titration. The following results were obtained:

Arsenious acid, $N/100$ solution Taken	Titration	Arsenious acid, $N/100$ solution Found	After deduction of blank
c.c.	c.c.	c.c.	c.c.
1·0	17·3 − 12·2 = 5·1	2·0	1·2
2·0	18·1 − 10·3 = 7·8	3·1	2·3
3·0	23·0 − 12·5 = 10·5	4·2	3·4
4·0	20·7 − 8·0 = 12·7	5·1	4·3
5·0	21·5 − 5·9 = 15·6	6·2	5·4
Blank	12·2 − 10·2 = 2·0	0·8	

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* Communication from the Research Department, Woolwich Arsenal

It is at once apparent that, although an end-point was now obtainable, the undesirable "blank" had reappeared. A trial of different filtering media did not lead to any improvement; asbestos gave a "blank" similar to that of paper pulp; glass wool did not retain the arsenic precipitate; different powders (*e.g.* sand, kieselguhr, etc.) either let the arsenic precipitate through, or else filtered with extreme slowness. I next tried to eliminate filtration altogether, and, with it, the blank due to the filter pulp, by shaking the precipitated arsenic out with benzene, separating the aqueous layer, and adding the standard iodine solution to the benzene suspension, when the arsenic dissolved with surprising promptness. The excess of iodine could now be titrated directly with arsenious oxide solution after the addition of sodium bicarbonate. This method, though interesting and having possibilities, gave uncertain and generally low results, probably owing to air-oxidation of the precipitated arsenic; with the higher amounts a trace, which had escaped extraction by the benzene, was often found in the aqueous layer. The following results were obtained:

	Arsenious acid, *N*/100 solution Taken	Titration	Arsenious acid, *N*/100 solution Found
	c.c.	c.c.	c.c.
(*a*)	1·00	9·7 − 7·1 = 2·6	1·04
(*b*)	1·00	14·3 − 11·9 = 2·4	0·96
(*c*)	2·00	14·5 − 9·3 = 5·2	2·08
(*d*)	4·00	14·5 − 5·4 = 9·1	3·64
(*e*)	5·00	19·6 − 8·0 = 11·6	4·64

In the case of (*d*), filtration of the aqueous layer yielded a minute amount of precipitated arsenic, which, on treatment, brought the amount of arsenic recovered up to 3·80 c.c. This method was abandoned.

As, however, the pulp used for filters quite obviously reacted with iodine, being stained an intense dark blue, wherein it differed from that used in the original investigation, it seemed probable that some reactive substance had been introduced in the manufacture and could be removed by suitable treatment. I found, on trial, that a thorough treatment with bromine removed all difficulty; on the other hand, the use of benzene as an indicator in the initial titration proved to be a definite improvement, and so was retained. The details of the process finally adopted are as follows:

PREPARATION OF PULP.—The pulp is prepared by shaking the torn-up filter paper with a mixture of 1 part of a saturated solution of bromine in hydrochloric acid, with 7 parts of water. When the paper is sufficiently disintegrated the flask is heated on the steam-bath for half-an-hour, and the liquid is then diluted with about its own volume of water, again shaken, and preserved in this state for use. When required for filtering an arsenic precipitate the filter is made in the ordinary way, thoroughly washed with water until perfectly white (*e.g.* 5 washings), and the liquid requiring filtration is then poured on to it.

TITRATION.—After the precipitate has been filtered off and washed, as already described (ANALYST, 1929, **54**, 523), the remaining wash-liquor is shaken out of the stem of the funnel, the funnel is inverted over a wide-mouthed beaker, and the filter is transferred to the beaker by inserting the jet of a wash-bottle into the stem of the funnel and blowing sharply; the sides and stem of the funnel having been rinsed into the beaker, an excess of standard iodine is immediately added, and the pulp is thoroughly broken up with a glass rod. After standing for a minute or two, about 5 c.c. of benzene are added, and the beaker is gently shaken; about 1 grm. of sodium bicarbonate is then added, and the liquid is immediately titrated with standard arsenious oxide solution until the aqueous liquid has turned completely white and the red colour of the benzene has started to fade; about 1 grm. of potassium iodide is now added, and the titration is continued, with vigorous shaking, until the benzene is quite decolorised, 2 to 3 drops being added in excess. The titration is finished in the way originally described, by adding a further 3 to 4 grms. of sodium bicarbonate, about 30 c.c. of water and a little starch solution, and titrating with standard iodine solution; it must be noted that the end-point, which is quite sharp, is brown and not blue. The calculation of results is as before, *i.e.* 1 c.c. of $N/100$ iodine used in dissolving the arsenic = 0·00015 grm. of arsenic. Results obtained by this method were as follows:

	Arsenious acid, $N/100$ solution Taken	Titration	Arsenious acid, $N/100$ solution Found
	c.c.	c.c.	c.c.
(*a*)	5·00	22·3 − 9·9 = 12·4	4·96
(*b*)	4·00	20·0 − 10·1 = 9·9	3·96
(*c*)	3·00	15·2 − 7·3 = 7·9	3·16
(*d*)	3·00	16·4 − 9·0 = 7·4	2·96
(*e*)	2·00	14·8 − 9·8 = 5·0	2·00
(*f*)	1·00	11·6 − 8·7 = 2·9	1·16
(*g*)	1·00	10·8 − 8·0 = 2·8	1·12

The slightly high results in (*c*), (*f*) and (*g*) are probably due to the presence of a rather large amount of hydrogen sulphide or sulphur dioxide in the air at the time the precipitates were being dissolved in iodine solution. A point that came to light during this investigation is that it is dangerous to let the precipitated arsenic stand longer than necessary, since it has a tendency to re-dissolve, owing, presumably, to air-oxidation.

The Determination of Minute Amounts of Copper in the Presence of Iron and Certain other Metals

By L. A. HADDOCK, B.Sc., A.I.C., and NORMAN EVERS, B.Sc., F.I.C.

(*Read at the Meeting, May* 4, 1932)

In 1908 Marcel Delépine published in the *Comptes rendus* (**146**, 981) a paper dealing with the properties of the metallic dithiocarbamates, including the copper salt, and in the same year he published a paper (*Bull. Soc. Chim.*, [IV], **3**, 652) on the detection of traces of copper and iron by means of a solution of a dialkyl dithiocarbamate.

Callan and Henderson (ANALYST, 1929, **54**, 650) applied the test quantitatively, and suggested the use of sodium diethyldithiocarbamate as a reagent for the determination of traces of copper. They stated that iron gives a brown colour with the reagent, which interferes with the copper colour, but that iron can be completely removed without loss of copper by precipitating it with ammonia as ferric hydroxide.

Grendel (*Pharm. Weekbl.*, 1930, **67**, 913, 1050, 1345) suggested the electrolytic deposition of the copper, solution of the deposit in acid, and repetition of the process to remove the last traces of iron. The copper is then determined in the solution by means of sodium diethyldithiocarbamate, the colour being shaken out with carbon tetrachloride and compared with the standard in a micro-colorimeter. Elvehjem and Lindow (*J. Biol. Chem.*, 1929, **81**, 435), in applying the copper pyridine thiocyanate method to the determination of minute amounts of copper, found it necessary to precipitate the copper as sulphide in order to avoid interference by iron. The method was also found unsuitable in the presence of calcium phosphate. Chalk (ANALYST, 1930, **55**, 187) found that this procedure was unnecessary, and that the addition of tartaric acid to the acid solution used in the copper pyridine thiocyanate test enabled the copper to be extracted by chloroform without interference from the iron. Ferrous salts, however, interfered with the reaction, and the method was not applicable in the presence of quantities of ferric iron greater than 40 mgrms.

I. DETERMINATION OF COPPER IN THE PRESENCE OF IRON.—The method which we suggest makes it possible to determine traces of copper in the presence of a large excess of iron without the necessity for the previous removal of the latter. This is effected by the addition of citric acid and ammonia to the solution containing the iron in the ferric condition. The reagent, a solution of sodium diethyldithiocarbamate, is then added, and the compound formed by the copper present with the reagent is extracted with carbon tetrachloride according to the method suggested by Grendel (*loc. cit.*). Under these conditions no interference by the iron occurs.

Callan and Henderson (*loc. cit.*) found it necessary to precipitate the iron as ferric hydroxide before determining the copper. They state that no copper remains in the precipitate of ferric hydroxide. Our experiments show that this is not the case, and that an appreciable proportion of the copper remains in the precipitate.

Elvehjem and Lindow (*loc. cit.*) separated the copper from iron by precipitation with hydrogen sulphide, but we have found that even this treatment does not remove the whole of the copper from the iron.

PROCEDURE.—Dissolve 2 grms. of citric acid (A.R.) in the solution containing the iron in the ferric condition and not more than 0·1 mgrm. of copper in a volume not exceeding 50 c.c. Add ammonia until the *p*H of the solution is not less than 9, and dilute to 70 c.c. Add 10 c.c. of a 0·1 per cent. solution of sodium diethyldithiocarbamate, and extract immediately by shaking with four successive quantities of 2·5 c.c. of carbon tetrachloride added from a burette, running off the lower layer into a stoppered cylinder. If the final extract shows not more than the faintest trace of colour, determine the colour of the mixed carbon tetrachloride extracts in a 1 cm. all-glass cell in a Lovibond tintometer, and read off the amount of copper from a curve based on Table I, using only the yellow constituent of the colour. If the final carbon tetrachloride extract shows more than a trace of colour, continue the extraction with further quantities of 2·5 c.c. of carbon tetrachloride until no further colour is removed. Make up the volume of the mixed extracts to 20 c.c., determine the colour as before, and read off the amount of copper from a curve based on Table II. If the colour now exceeds 10 yellow units, too much copper has been taken, and the method must be repeated on a smaller quantity.

Standard colours containing known amounts of copper may be prepared by adding quantities of a solution containing 0·001 per cent. of copper to the alkaline solution in the separator after the copper previously present has been removed, and extracting in the manner described above. Comparisons may be made in a colorimeter or by direct comparison in tubes.

A control must be carried out in all cases with all the reagents, and the amount of copper found must be subtracted from the result.

NOTES ON THE METHOD.—All reagents should be as free from copper as possible in order to avoid a high blank subtraction.

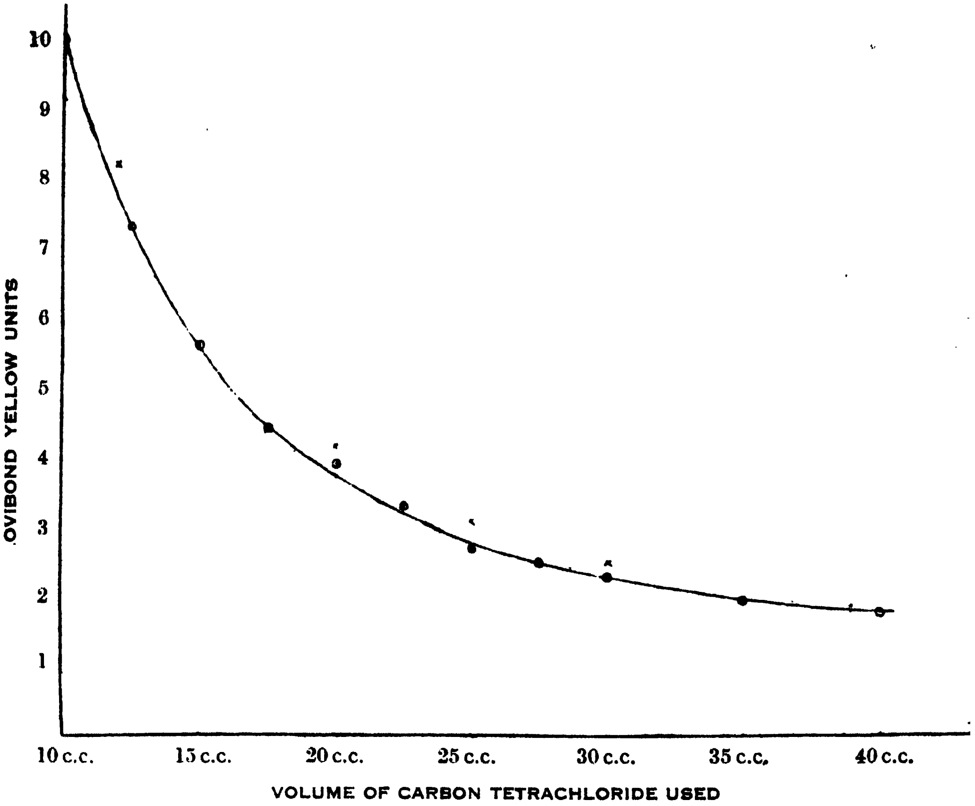
Ferrous iron in quantities exceeding 1 mgrm. should be absent.

Two grms. of citric acid are sufficient for quantities of iron up to 0·1 grm. If the iron exceeds this amount, the citric acid must be increased proportionally.

Provided that the *p*H of the solution is not less than 9, a moderate excess of ammonia does not affect the results.

The following substances did not interfere with the method: Alkali metals, nitrates in amounts equivalent to 0·75 mgrm. of NO_3, sodium phosphate equivalent to 0·25 grm. of P_2O_5, calcium phosphate equivalent to 0·3 grm. of $Ca_3(PO_4)_2$. In the presence of calcium phosphate the *p*H should be approximately 9 and should not exceed that value, otherwise precipitation will occur. In the absence of iron, sulphurous acid, equivalent to 0·5 grm. of SO_2, did not interfere. Quantities as low as 0·005 mgrm. of copper may be determined in the presence of as much as 0·25 grm. of iron, *i.e.* 0·002 per cent.

The colour is permanent for at least one hour; some fading occurs after four hours. The depth of the colour is not proportional to the concentration of copper; the relation is shown in the accompanying curve.



The points marked ○ on this curve were obtained by direct dilution with carbon tetrachloride of a solution giving 10 yellow units initially. The points marked * were obtained by extraction of known amounts of copper from the citrate solution. This shows that the dilution of a solution of the copper compound gives the same colour values as the same concentrations of copper when extracted directly, *e.g.* 0·05 mgrm. of copper was extracted with four quantities of 2·5 c.c. of carbon tetrachloride. The reading was 8·2 units. After dilution to 20 c.c. with carbon tetrachloride the reading was 3·1 units. The same quantity of copper was extracted with four quantities of 5 c.c. of carbon tetrachloride; the reading was again 3·1.

Curves were constructed by adding known amounts of copper to the copper-free ammoniacal citrate solutions containing the reagent. The following results were obtained:

TABLE I

Volume of carbon tetrachloride, 10 c.c.

Copper added Mgrm.	Colour Lovibond units Yellow
0·005	0·7
0·01	1·2
0·02	2·5
0·03	4·2
0·04	6·4
0·05	8·2

TABLE II

Volume of carbon tetrachloride, 20 c.c.

Copper added Mgrm.	Colour Lovibond units Yellow
0·05	3·1
0·06	4·2
0·07	5·1
0·08	6·3
0·09	7·4
0·10	8·3

These results were repeated in the presence of amounts of iron up to 0·25 grm. without altering the figures.

In order to confirm the fact that the presence of iron has no effect, quantities of ferric chloride were taken and the copper present was determined. Known amounts of copper were added, and the total copper was determined. The results are given in Table III.

TABLE III

Ferric chloride ($FeCl_3.6H_2O$) Grm.	Copper present Mgrm.	Copper added Mgrm.	Total copper found Mgrm.
0·5	0·022	0·010	0·031
0·5	0·022	0·020	0·041
0·6	0·055	0·030	0·088
0·6	0·055	0·005	0·059
1·0	0·008	0·010	0·018

ADSORPTION OF COPPER BY FERRIC HYDROXIDE.—The iron was precipitated from solutions of ferric chloride by the addition of ammonia. The precipitate was washed thoroughly, and the copper was determined both in the precipitate and in the filtrate.

Ferric chloride ($FeCl_3.6H_2O$) Grm.	Total copper present Mgrm.	Copper in precipitate Mgrm.	Copper in filtrate Mgrm.
1·0	0·022	0·014	0·007
0·6	0·055	0·050	0·006

PRECIPITATION OF COPPER BY HYDROGEN SULPHIDE.—(*a*) *In the absence of Iron.*—Fifty c.c. of a copper sulphate solution containing 0·5 mgrm. of copper were brought to *p*H 3·5 with dilute hydrochloric acid, the solution was boiled, and a current of hydrogen sulphide was then passed through it until it was cool. After filtration of the liquid through copper-free asbestos until colourless, the filtrate contained 0·022 mgrm. of copper.

(*b*) *In the presence of Iron.*—About 5 grms. of iron wire were dissolved in a slight excess of hydrochloric acid, the solution was diluted to about 100 c.c. with water and saturated with hydrogen sulphide, and the precipitate was filtered off through a copper-free sintered glass crucible. The filtrate was oxidised by boiling with a little nitric acid and evaporated to dryness. The copper found in the residue was 0·01 mgrm. per grm., and in a second experiment 0·02 mgrm. per grm. A further experiment was carried out in the same way, but with the solution kept at *p*H 3·5 during the precipitation. The copper found was 0·008 mgrm. per grm.

DETERMINATION OF COPPER IN THE PRESENCE OF OTHER METALS.—*Aluminium and Zinc.*—The same method works well in the presence of aluminium and zinc in quantities up to 0·2 grm. of aluminium or 0·1 grm. of zinc. In the absence of iron the aluminium or zinc may be dissolved in excess of sodium hydroxide solution with the addition of ammonia. On adding the reagent and extracting with carbon tetrachloride in the same way, results were obtained comparable with those obtained in the presence of iron, but with even larger quantities of aluminium and zinc (up to 0·5 grm. may be used).

Chromium.—The chromium must be in the chromic condition. If not, the solution must be reduced by the addition of sulphurous acid until no colour is given when a solution of diphenylamine in sulphuric acid is used as an external indicator. The solution is heated to boiling with 2 grms. of citric acid, and, after cooling, excess of ammonia is added. If the preliminary boiling is not carried out, chromium hydroxide is precipitated. The method may then be completed as described above. Amounts of chromium up to 0·2 grm. may be present.

Manganese.—If no more than a trace of iron is present, the copper may be determined in the presence of manganese (up to 0·2 grm.) by adding 2 grms. of citric acid and 5 c.c. of a 5 per cent. solution of sulphur dioxide, followed by excess of ammonia. A faint pink colour is extracted from solutions containing manganese, but the copper is still proportional to the yellow constituent in the Lovibond tintometer.

Tin.—In the absence of iron, traces of copper may be determined in the presence of stannic salts by the addition of an excess of sodium hydroxide and ammonia in the same way as described under aluminium and zinc.

Our thanks are due to Messrs. Allen & Hanburys, in whose laboratories this work was carried out.

The Determination of Silicon in Aluminium

By L. H. CALLENDAR, Ph.D., F.I.C., A.R.C.S.

In analysing commercial aluminium it is customary to determine silicon and iron only, and not to determine other impurities, when, as is usually the case, they are present in quantities of less than 0·01 per cent. Of these standard determinations that of silicon is the more important, not only because it occupies most of the time of the analyst concerned with aluminium, but also because the solubility of silicon in aluminium (iron is practically insoluble) causes variations in the mechanical, physical and electrical properties of the metal. More recently the extensive use of aluminium-silicon alloys has added further interest to the question.

As the result of experience in the metallurgical laboratories of the British Aluminium Company, it has been found that, for accurate analysis, the best results are obtained by a method in which the metal is dissolved in soda solution, and the silica then separated by acid; the older processes in which the metal is dissolved directly in mixed acids give low results, owing to the loss of volatile silicon compounds during solution of the metal.

In this paper it is proposed first to examine the main errors which are liable to occur in all the commonly used methods for the determination of silicon in aluminium, to show by experimental results the conditions under which these errors can be reduced to a minimum, then to give the experimental details of the procedures which have been found best for the four principal methods, and also to provide some guidance as to the choice of method for accurate and routine analyses of pure metal and aluminium-silicon alloys.

Conditions of Ignition for Obtaining Non-hygroscopic Silica Residues.—The most common causes of high results in silicon analysis are incomplete ignition of the silica residue and absorption of moisture by the residue before and during the weighing operations. As the available information in the literature was contradictory and inexact, experiments were carried out to determine the best conditions for the ignition of silica residues obtained during the analysis of aluminium and aluminium-silicon alloys.

The results in Table I are for silica residues from an aluminium-silicon alloy analysed by the soda method (for full experimental details, see Method A, p. 506), and the results in Table II are those obtained with mixed residues from commercial aluminium analysed by the mixed acid process (see Method B). The ignitions were carried out in porcelain crucibles, a blank crucible being heated alongside to check any changes in weight of the crucible. The temperature of the muffle furnace used was determined by means of thermo-couples inserted alongside the crucibles.

TABLE I

TEMPERATURE OF IGNITION AND MOISTURE-ABSORPTION OF SILICA RESIDUES

Exp. No.	Temperature and duration of ignition	First weight of ignited residue	Moisture-absorption after standing 3 days in open air	Loss of weight on 2nd ignition at 900° C. for 30 mins.	Moisture-absorption after again standing in air for 18 hours
	° C.	Grm.	Grm.	Grm.	
970	400–600° Rising in 30 min.	0·1177	0·0147	0·0199	Nil
971		0·1136	0·0140	0·0187	Nil
972	600–700° Rising in 30 mins.	0·1095	0·0020	0·0096	Nil
973		0·1167	0·0103	0·0160	Nil
974	700–800° Rising in 30 mins.	0·1143	0·0101	0·0153	Nil
975		0·1163	0·0072	0·0146	Nil
965	800–1000° Rising in 40 mins.	0·1123	Nil	0·0004	Nil
977		0·1101	Nil	0·0021	Nil

TABLE II

INCOMPLETE IGNITION OF SILICA RESIDUES

Exp. No.	Temperature and duration of ignition	Weight after ignition	Re-ignition temperature	Weight after re-ignition	Loss per cent.
		Grm.	° C.	Grm.	
2634	770–800 °C. for about 30 mins.	0·0698	900° for 1 hour	0·0646	7·5
2634		0·0718		0·0668	7·0
2632		0·0414		0·0374	9·7
2632		0·0414		0·0376	9·2
2635		0·1010		0·0964	4·7
2637		0·0992		0·0918	7·5
2638		0·1006		0·0922	8·4

As the results given in Tables I and II are evidently of the first importance for obtaining accurate results in the determination of silicon, some confirmatory experiments were carried out. For these experiments some 60 silica residues were collected from routine analyses of commercial aluminium by the mixed acid process, and were well mixed together, and about 0·1 grm. of the mixture was weighed out into each of 4 platinum crucibles. In a further series the residues from a number of analyses of aluminium-silicon alloy by the soda process were also collected and mixed, and they were weighed into another series of platinum crucibles; they were then ignited for 1 hour at 850° to 950° C., exposed to the air for 2 hours, and weighed. A comparison of the residues from the two processes showed that the amounts of moisture absorbed by the ignited residues ranged from *nil* to 0·0003 grm.

In actual practice it is unlikely that the silica residues would be exposed to the air for as long as half-an-hour before and during weighing.

The results given in Tables I and II indicate that these silica residues require to be heated at 900° C. for about 1 hour to ensure their dehydration and to render them non-hygroscopic. If the residues are heated in porcelain crucibles the temperature of the muffle furnace should not be allowed to rise above 1000° C., as small residues are liable to become fused into the bottom of even the best porcelain crucibles. Some of the results indicated that there is a slight tendency for residues from the mixed acid routine process to absorb moisture, even after 1 hour's ignition at 900° C. This is due to the presence in these residues of 6 to 8 per cent. of alumina (about 5 times as much alumina as is contained in the residues from the soda method), which is more difficult to render non-hygroscopic than the silica itself. As the moisture absorbed in these experiments amounts to only 0·2 per cent. of the weight taken, the error introduced would obviously be quite negligible in the routine analysis of commercial aluminium, in which the average silicon content might be of the order of 0·20 per cent. For the most accurate analysis, however, especially with large silica residues, it is advisable after 1 hour's ignition at 900° C., to re-ignite the residue for half-an-hour, and, if the further loss of weight is then inappreciable, the amount of silicon in the residue may be determined by treatment with hydrofluoric acid.

USE OF HYDROFLUORIC ACID METHOD FOR DETERMINING SILICA IN RESIDUES.—Although, in general, this process is well known, it is advisable to point out certain errors to which it has been found liable in the particular case of the determination of silica in siliceous residues from aluminium.

The usual procedure is as follows:—The siliceous residue left after ignition in a platinum crucible is treated with a few drops of concentrated sulphuric acid, and then with 1 to 2 c.c. of hydrofluoric acid. The crucible is very carefully warmed until all the acid has been expelled, after which it is ignited for a few minutes and allowed to cool, and the process is repeated until a constant weight is obtained. The loss of weight is taken as the silica in the residue.

The chief source of error is the presence of alumina in the residue. In the "fuming" process this alumina appears to be partly converted into aluminium sulphate, which is not completely decomposed by the subsequent ignition; this makes the silicon results too low. It was found from a number of experiments that to ensure decomposition into Al_2O_3, it is necessary to heat the residue at 1000° C. for about 10 minutes, after the treatment with hydrofluoric acid.

Errors due to impurities in the hydrofluoric acid itself can be avoided by making a simultaneous blank determination. Residues contaminated with vanadium oxide from a vanadium aluminium alloy must be heated with hydrofluoric acid and freed from sulphuric acid on the hot plate before being heated over a flame. Residues which are brown in colour, owing to the presence of silicon, require special treatment.

TREATMENT OF BROWN SILICEOUS RESIDUES FROM ACID PROCESSES.—In the method proposed by Regelsberger, in 1891, the silica and silicon are determined separately by a double process of heating, first with hydrofluoric and sulphuric acids (the loss of weight being taken as equal to the silica in the original residue) and then with a mixture of hydrofluoric and nitric acids, the loss of weight obtained being assumed to be equivalent to the silicon in the original residue. This process has been advocated by W. H. Withey (*J. Inst. Metals*, **1916**, **15**, **207**), and by the American Society for Testing Materials for the determination of graphitic silicon in aluminium; further, it has been used by Honigschmidt in his attempts to prove the existence of silicon sub-oxides (*Ber.*, **1909**, **118**, 289), and it is included in many modern textbooks. Experimental results obtained at the Warrington laboratory tend to show that this process is not only inaccurate, but also quite useless for the determination of silica or silicon in a mixture of the two. The cause of the inaccuracy of the process is that in the first heating with acid and ignition part of the silicon is oxidised to silica, and in subsequent repetitions of the process this silica is volatilised by the hydrofluoric acid, and so on until all the silicon is volatilised, without the use of nitric acid at all; moreover, according to Manchot (*Ber.*, 1921, **54**, 3107), silicon itself is directly attacked by hydrofluoric acid *plus* sulphuric acid, and some may be lost as silicon fluoride.

This loss of silicon by heating with hydrofluoric acid *plus* sulphuric acid alone is illustrated by the results given in Table III; these results are merely typical of many obtained in this laboratory.

For the first experiments pure silicon was prepared from crystalline material by the N.P.L. method (N. P. Tucker, *J. Iron Steel Inst.*, 1927, **115**, 142); the results of the first four treatments with two samples of this material with hydrofluoric acid *plus* sulphuric acid are shown in the table; after ten further treatments the material continued to lose weight at much the same rate. A sample of so-called pure amorphous silicon, obtained from a well-known supplier, was treated in the same way; after five heatings this material ceased to lose weight, and the brown residue was found to consist only of iron oxide and alumina, all the silicon originally present having been expelled. The second series of results in Table III was obtained with dark brown siliceous residues from low-purity aluminium; after 2 to 3 treatments these residues became colourless, and the residual powder was pure alumina. It should be added that no nitric acid could be detected in the hydrofluoric and sulphuric acids used in all our experiments.

TABLE III

LOSS OF SILICON ON TREATMENT WITH HYDROFLUORIC ACID

Sample	Weight Grm.	First loss Grm.	Second loss Grm.	Third loss Grm.	Fourth loss Grm.
Pure cryst. silicon	0·1000	0·0021	0·0010	0·0010	0·0029
	0·0657	0·0018	0·0030	0·0040	0·0018
Brown siliceous residues from aluminium	0·0134	0·0110	0·0014	Nil	Residues quite white, only Al_2O_3 left
	0·0127	0·0103	0·0022	Nil	
	0·0196	0·0146	0·0015	0·0014	

From these results it is clear that Regelberger's method is of no use whatever for the determination of silicon and silica in a mixture of the two. (R. L. Johnston, *Chemist-Analyst*, **1924**, **41**, **9**; D. von Prettner, *Chem. Ztg.*, 1927, 261.)

A satisfactory procedure for the treatment of siliceous residues containing silicon was proposed by Hunt, Clapp and Handy in 1892 (*J. Anal. Appl. Chem.*, 1892, 6, No. 1; see also H. J. Williams, *Trans. Amer. Inst. Min. Eng.*, 1888, 17, 542). They suggested that the brown residues should be fused with sodium carbonate, and that the silicon, being oxidised to silica, should then be separated by treatment with excess of acid as usual. A simpler and more convenient procedure is to treat the residues by the soda method (Method A).

If the aluminium metal is known to contain much free silicon, half the time of the analysis may be saved by dissolving the metal in sodium hydroxide solution instead of acid at the outset and proceeding by the usual soda method.

IMPURITIES IN SILICEOUS RESIDUES.—As has been pointed out, the siliceous residues obtained from aluminium by any of the methods of separation discussed in this paper contain variable amounts of impurities (mainly Al_2O_3). The percentage of impurities varies from about 1 per cent. for residues from 10 per cent. silicon alloys, to 6–10 per cent. for residues from commercial metal, and it cannot be reduced in either case without seriously increasing the loss of silica in the filtrates and wash-water.

LOSS OF SILICA IN THE FILTRATES.—The question of the loss of silica in the filtrates in different methods of determining silicon in iron and steel and ferro-silicon has frequently been investigated, more particularly by Stadeler (*Stahl und Eisen*, 1927, 47, 966; *Archiv für das Eisenhüttenwesen*, 1929, 2, 425), who gives many hundreds of results obtained from eleven different laboratories by means of sixteen different methods of analysis. The results given here are some of those obtained in the determination of silicon in aluminium by the mixed acid process and by the soda process.

TABLE IV

ANALYSIS OF H.P. CAST METAL BY MIXED ACID PROCESS

Exp. No.	Material	Residue Grm.	Silica by treatment with HF Grm.	Residue from filtrate Grm.	Silica Grm.	Second filtrate Grm.	Silica Grm.	Total silica Grm.	Nett silicon Per Cent.
1100–1	10 grms. of Hoope's American metal (duplicates)	0·0117	0·0109	0·0012	0·0010	Mean nett SiO_2 =0·0002		0·0121	0·0544
1102–3		0·0114	0·0104	0·0017	0·0015			0·0121	
1104–5	Blanks on reagents	0·0001	0·0001	0·0003	0·0002	Nil		0·0003	Blank SiO_2 mean = 0·00045
1106–7		0·0002	0·0002	0·0005	0·0004			0·0006	
1042	5 grms. of Hoope's American metal	0·0052	0·0047	Approximate analysis, neglecting filtrate losses and blanks.					0·045
1043		0·0052	0·0049						
1070	10 grms. of Foyer's 99·8 per cent. metal	0·0208	0·0185	0·0020	0·0010	0·0008	0·0006	0·0201	0·0888
1071		0·0202	0·0183	0·0021	0·0011	0·0008	0·0003	0·0197	
1075	Blanks on reagents	0·0009	0·0007	0·0008	0·0002	0·0006	0·0003	0·0012	Mean b SiO_2=0
1076		0·0013	0·0006	0·0007	Nil	0·0003	Nil	0·0006	
1044	5 grms. of Foyer's 99·8 per cent. metal	0·0092	0·0090	Routine analysis correcting for filtrate losses by the use of the factor 48·5 (see p. 505)					0·088
1045		0·0096	0·0091						

The first results given in Table IV show typical filtrate losses found by the mixed acid process in the analysis of high-purity cast metal, the analysis being carried out according to the details given in Method B; in each case the residues obtained were quite white, and the silica was determined directly by heating them with hydrofluoric acid. The experiments 1042–3 show the large error introduced into the results by neglecting the filtrate losses.

Results showing typical filtrate losses with the soda method are given in Table V; these are results of duplicate determinations on commercial metal and aluminium-silicon alloys. From the mean of these filtrate losses a factor can be calculated which may be used in routine analysis to avoid the lengthy re-evaporation of the filtrates; this factor is given in the last column of the table. In these experiments the mean filtrate loss works out at 3·24 per cent.

TABLE V

STANDARD SODA METHOD

CORRECTIONS FOR NORMAL SILICON LOSS IN FILTRATION

Exp. No.	Weight of metal taken Grm.	Silica in residue A after treatment with HF. Figure corrected for SiO_2 in blank Grm.	Filtrate silica 1st & 2nd filtrate residues corrected, etc. Grm.	Total silica from metal Grm.	Filtrate loss Per Cent.	Corrected factor (× SiO_2 in 1st residue, A = silicon in metal) Per Cent.
1160–1	1	0·0038	0·0001	0·0039	2·6	48·3
1162–3	,,	0·0053	0·0002	0·0055	3·6	48·8
1110–1	,,	0·0070	0·0003	0·0073	4·1	49·0
1009–10	,,	0·0099	0·0003	0·0102	2·9	48·4
1166–7	,,	0·0121	0·0004	0·0125	3·2	48·5
1168–9	,,	0·0163	0·0006	0·0169	3·5	48·7
1117–8	,,	0·0228	0·0010	0·0238	4·2	49·1
1013–4	,,	0·0590	0·0024	0·0614	3·9	48·9
1015–6	,,	0·1151	0·0031	0·1182	2·6	48·3
940–1	0·5	0·0690	0·0021	0·0711	3·0	96·8
1130–1	,,	0·0975	0·0029	0·1005	2·9	96·8
942–3	,,	0·1206	0·0029	0·1235	2·4	96·2

Mean factor for 1 grm. of metal = 48·5

It has often been stated that filtrate losses can be prevented or greatly reduced by the use of pulp-pad filters; the experimental results given below show, however, that there is little difference between the filtrate losses of silica obtained with pulp-pad filters and the losses obtained with papers of good quality. The results of a comparison between a loose pulp pad (for this the pulp was merely poured into the funnel without any pressing down), a tight pad well pressed down, and Schleicher and Schüll papers of four different textures are given in Table VI. The results are the mean of duplicate determinations.

TABLE VI

COMPARISON OF FILTER PAPERS AND PULP PADS

Exp.	Filter medium	Total silica Grm.	Filtrate loss Per Cent.
12–13	Pulp pad, loose	0·0717	4·0
10–11	Pulp pad, tight	0·0717	3·6
14–15	Paper coarse S. & S. 589, black	0·0721	3·5
16–17	Paper medium 589, white	0·0716	3·0
18–19	Paper fine 589, blue	0·0719	3·1

The results in Table VI seem to indicate a slight advantage in the use of medium filter paper for accurate work; for routine work the pulp pads offer considerable advantages, as they are easier to wash, and tend to accelerate the filtration.

Large variations in the amount of filtrate loss are primarily due to the *time* taken in boiling with water after the first dehydration of the silica with sulphuric acid. By varying this time from 1 minute to 30 minutes the filtrate loss has been found to vary from 1 to 5 per cent., while at the same time the alumina-content of a large residue may vary from 5 to 10 per cent. The results of a large number of experiments have shown that boiling for about 15 minutes gives a nearly uniform filtrate loss of about 3 per cent. (with Schleicher and Schüll medium papers), with a residue containing minimum amounts of alumina. The actual time, beyond 5 to 10 minutes, during which the residue is heated after being evaporated with sulphuric acid until fumes appear, does not appear to influence the filtrate losses, but very prolonged treatment increases the amount of alumina in the residue, and is, therefore, disadvantageous.

EXPERIMENTAL DETAILS OF METHODS.—The experimental details of the four principal methods which have been used for the determination of silicon in aluminium are those which have been found to be best from experience in a laboratory where some 10,000 silicon determinations on aluminium and its alloys are carried out every year.

METHOD A—SODA METHOD

The metal is dissolved in 10 per cent. caustic soda solution in a covered nickel crucible, and the liquid is boiled, diluted and poured into excess of 60 per cent. sulphuric acid. It is then evaporated until fumes appear and diluted, and the silica is filtered off and determined.

The quantities of alkali, acid, etc., required for different classes of metal are given in the Table VII.

TABLE VII

QUANTITIES USED IN SODA METHOD FOR SILICON DETERMINATION

Metal with silicon content Per Cent.	Weight of metal Grms.	Volume of 10 per cent. soda solution c.c.	Volume of 60 per cent. sulphuric acid c.c.
0·05 to 0·15	5	100*	180
0·15 to 0·50	2	50	100
0·4 to 5	1	30	60
2 to 15	0·5	20	35
12 to 25	0·25	20	35

* Nickel crucibles of one-litre capacity may be used for metal of high purity, though the silicon in this class of metal is more conveniently determined by the sulpho-nitric acid process (Method C).

Experimental Details.—Weigh out 1 grm. of millings (*e.g.* of metal containing about 1 per cent. of silicon) into a 200-c.c. nickel crucible, add 30 c.c. of freshly-prepared 10 per cent. sodium hydroxide solution and cover the crucible with the lid. When nearly all the metal has dissolved, wash down the lid and sides of the crucible with a very little hot water, replace the lid, and boil the liquid briskly on the hot plate for about 10 minutes, just avoiding evaporation to complete dryness. Remove the crucible from the plate, wash down the lid and sides, dilute the liquid to about 40 c.c., boil until most of the residue is detached from the bottom of the crucible; then transfer the contents to a 400-c.c. shallow beaker, already containing 55 c.c. of 60 per cent. sulphuric acid, and add the aluminate solution to the acid, meanwhile rotating the beaker.

Wash out the crucible with 5 c.c. of 60 per cent. sulphuric acid, and then with hot water, finally removing any silica particles adhering to the side and lid by means of a rod tipped with rubber. Cover the beaker with a clock-glass and evaporate the liquid rapidly on the hot plate, carefully avoiding spurting; heat until strong fumes appear, and continue the heating for 15 minutes.

Remove the beaker from the plate, allow the residue to cool a little, add from a wash-bottle (keeping the cover-glass still on the beaker) a fine stream of cold water (just a few c.c. to break up the cake), and then wash down the cover-glass and sides of the beaker with cold water. Add about 150 c.c. of hot water, stir with a rod tipped with rubber to detach the cake and prevent bumping, heat to boiling, and boil gently for 15 minutes. Filter on a Schleicher and Schüll medium paper (589 white band) or on a pulp pad. Wash out the beaker with hot water, remove any adhering silica, and then wash the filter pad twice with hot water.

Wash the residue on the filter three times with hot dilute (1:3) hydrochloric acid, allowing the filter to drain after each addition of acid, and then wash 8 to 10 times with hot water, testing the final filtrate for chlorides with silver nitrate solution. Transfer the paper or pad to a platinum crucible, dry on the hot plate, then transfer to a muffle furnace, ignite for 1 hour at 900° C., cool for 1 hour in a desiccator, and weigh. Re-ignite for 15 minutes over a blast lamp, cool and weigh. If this second loss of weight is inappreciable, as it usually is, the residue is now ready for heating with hydrofluoric acid.

To the platinum crucible add 4 drops of concentrated sulphuric acid and about 1 c.c. of hydrofluoric acid, replace the lid and evaporate the liquid carefully over a very low flame in a fume-cupboard. When no more fumes are evolved, ignite the crucible and its contents over a blast-lamp for 10 minutes, cool and weigh. Repeat the treatment with hydrofluoric acid, adding this time 2 drops of sulphuric acid and 0·5 c.c. of hydrofluoric acid, evaporate, ignite, cool and weigh. If the change of weight is inappreciable, further treatment with hydrofluoric acid is unnecessary. The loss of weight represents the pure silica in the residue, after a correction has been made for impurities in the hydrofluoric and sulphuric acids.

For accurate analysis, blank determinations must always be made. The filtrates from the first filtration, which contain about 3 per cent. of the total silica, must be evaporated again after the addition of 10 c.c. of 60 per cent. sulphuric acid; the filtrates obtained after this treatment may also be treated to recover any silica they may contain, but usually the amount recovered here is not appreciably greater than that found in the blank determination. The silica recovered from the filtrates may be added to the main bulk, and submitted with it to the treatment with hydrofluoric acid. (Total silica 0·4672 = silicon.)

ROUTINE ANALYSIS OF METAL OF KNOWN ORIGIN.—In this case the analysis can be greatly shortened by omitting the re-ignition of the silica residue, and also the heating with hydrofluoric acid, the correction to the results to allow for these omissions being found by re-igniting a number of residues and then heating them with hydrofluoric acid (in the routine analysis of 10 per cent. silicon alloy I have used a correction figure of 0·0015 grm.). The analysis can be further shortened by omitting the recovery of silica from the filtrates and making an allowance for this by calculating the SiO_2 to Si by the corrected factor 0·485, obtained as a mean of the results in Table V.

NOTES.—The 10 per cent. sodium hydroxide solution should be freshly prepared in a nickel basin or crucible. A nickel rod may be used for mixing the solution, which should be measured out in a nickel cylinder, and the reaction crucible and its lid should be handled with nickel tongs.

With silicon-aluminium alloys (*e.g.* the common 10 to 14 per cent. alloys) after evaporation of the soda solution the residue in the crucible should contain no visible brown particles; if, however, it is brownish, the soda should be diluted with about 10 c.c. of hot water, and boiled again for a few minutes to complete the conversion of the silicon into silica.

After having cooled down somewhat after the heating with sulphuric acid, the contents of the beaker should be diluted with a little *cold* water, as this throws out the silica in a granular form suitable for filtration, and also avoids spurting.

This soda method is especially suitable for the accurate or routine analysis of low-purity metal and aluminium-silicon alloys.

METHOD B—MIXED ACID PROCESS

The metal is dissolved in a dilute acid mixture ($HCl+HNO_3+H_2SO_4$). The liquid is evaporated until it fumes strongly, and the silica is separated as usual. The residue may then be fused with fusion mixture ($Na_2CO_3+K_2CO_3$), the fused mass is treated with excess of acid, the solution is evaporated until fumes appear, and the silica is separated as before. In either case the final residue is determined by evaporation with hydrofluoric acid (*cf.* F. Regelsberger, *Z. angew. Chem.*, 1891, 1, 442; *Amer. Soc. Test. Mat.*, *Tentative Standards*, 1928, p. 782).

The acid mixture which has been found most convenient for routine determinations of silicon is as follows:—

675 c.c. of sulphuric acid of sp.gr., 1·84
338 c.c. of nitric acid of ,, 1·42
338 c.c. of hydrochloric acid of ,, 1·16
3150 c.c. of distilled water.

EXPERIMENTAL DETAILS (FOR COMMERCIAL METAL).—Weigh out 1 grm. of millings into a 400-c.c. shallow beaker, add 35 c.c. of acid mixture, and cover with a clock-glass. Warm on the hot plate until the action starts, remove and let the action continue until the metal is practically dissolved. Wash down the cover glass and sides of the beaker with hot water, transfer the beaker to the hot plate and evaporate until fuming begins, care being taken to avoid spurting. Transfer the beaker to the cooler part of the plate and allow the acid to fume strongly for 10 to 15 minutes.

Then proceed exactly as with the soda method (Method A), filtering off the silica on a paper-pulp pad. After washing as before, dry the pulp pad by means of suction with the aid of the filter pump, transfer the pad to a porcelain crucible by means of tongs, removing all traces of silica adhering to the funnel with moistened filter paper, which is added to the main residue in the crucible.

Ignite in a muffle furnace and burn off the filter paper, allow the crucible to cool, transfer the residue to a nickel crucible, and mix it with eight times its amount of pure fusion mixture. Heat the mixture to fusion and continue heating until the liquid appears fairly transparent and clear. Cool quickly in cold water to crack the cake, transfer this to a 400-c.c. beaker containing a little hot water, and rinse the nickel crucible into the beaker.

Add 60 per cent. sulphuric acid gradually to the contents of the beaker, until acid to litmus, and finally add about 20 c.c. in excess. Evaporate until the acid fumes strongly, take up the residue, filter, and wash as in the soda method. Ignite the final residue to constant weight at 900° C., and determine the silica by the usual treatment with hydrofluoric acid.

This method is unsuitable for analyses where a high order of accuracy is imperative, owing to the loss of volatile silicon compounds during the solution of the metal.* It has the further disadvantages of taking about twice as long as the soda method, and of being subject to double filtration losses.

ROUTINE ANALYSIS.—The mixed acid process is convenient for the routine determination of silicon in commercial aluminium. By the use of the modified factor referred to above the process can be greatly shortened and made sufficiently accurate for industrial purposes, when the conditions under which the metal is produced are more or less constant, as, of course, they usually are in any large-scale production.

For routine analysis of commercial cast metal, the first silica residue is ignited for about 1 hour at 850–950° C.; after cooling in a desiccator, it is weighed, and the weight obtained is multiplied by the empirical laboratory factor to obtain the percentage of silicon. I have found in practice that a factor of 48 for the routine mixed acid process gives results which agree well with those obtained by the soda method with pure cast metal.

It is, however, advisable for other laboratories wishing to use the mixed acid process for routine analysis, to determine their own factors by comparing the results of, say, six duplicate analyses by different operators of a dozen different samples of metal by the mixed acid process with accurate analyses of the same samples by the soda method. Even then, the routine process is not suitable for the determination of silicon in metal which has been heat-treated at a low temperature (300° C.) so as to throw most of the silicon out of solution, or at a high temperature (550° C.), so as to bring the silicon into solid solution. Such metal should be analysed by the soda method or by the sulpho-nitric acid process, with re-annealing if necessary.

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* The experimental evidence on which this statement is based forms part of the subject-matter of another paper to be published shortly. In the meantime it may be said that the evidence of several hundred experiments shows that the mixed acid process almost always gives low results, as compared with the soda method, and that this difference has been found to be due solely to the loss of volatile silicon compounds.

METHOD C—SULPHO-NITRIC ACID METHOD

The metal is annealed for 2 to 12 hours at 570° C., and then quenched in cold water. It is dissolved in a mixture of concentrated nitric acid and 60 per cent. sulphuric acid. After solution, the silica is separated by the usual method, and, after ignition, the white residue is treated with hydrofluoric acid to determine the silica.

EXPERIMENTAL DETAILS.*—Dissolve 5 grms. of millings in duplicate in 1500-c.c. shallow beakers in 150 c.c. of a mixture of sulphuric and nitric acids (60 c.c. of 60 per cent. sulphuric + 40 c.c. of concentrated nitric acid). Evaporate down carefully to avoid spurting. Heat in the usual way until fumes appear.

Then remove the beakers from the plate and allow them to cool for 5 to 10 minutes before diluting the liquid very carefully with a thin stream of water from the wash-bottle. Dilute to about 700 c.c., filter on a Schleicher and Schüll paper, No. 589/2, and wash the residues as usual. Dry and ignite the residues in platinum crucibles at 900° C. until constant in weight. Heat with hydrofluoric acid as in the soda method to determine the silica.

Collect the filtrates, add 10 c.c. of 60 per cent. sulphuric acid, heat until the acid fumes strongly, dilute, boil, filter, ignite, and treat with hydrofluoric acid. Blank determinations should be made at the same time.

$$\begin{aligned} \text{Silicon} &= \text{SiO}_2 \text{ in 1st residue} \times 0{\cdot}485 \ldots\ldots\ldots\ldots & (1)\\ &= \text{1st+2nd} \quad ,, \quad \times 0{\cdot}470 \ldots\ldots\ldots\ldots & (2)\\ &= \text{1st+2nd+3rd} \;,, \quad \times 0{\cdot}4672 \ldots\ldots\ldots\ldots & (3) \end{aligned}$$

By applying the factor 0·47 to the weight of the silica found in the first and second residues, the results obtained by this method agree very closely with those obtained by the soda method.

This sulpho-nitric acid process is somewhat more convenient than the soda process for the determination of silicon in high-purity metal. For routine analysis of commercial metal, it is not so safe in the hands of less experienced workers as the mixed acid process, owing to the high concentration of acid used.

METHOD D—SULPHURIC ACID PROCESS

The metal is dissolved in sulphuric acid (sp.gr. 1·6), the solution is filtered without being heated until it fumes, and the siliceous residue is ignited directly and weighed. (*Cf.* F. Ahrens, *Chem. Tech. Analyses*, 1901.)

EXPERIMENTAL DETAILS.—In the case of commercial metal, 3 grms. of the sample are weighed out into a 500-c.c. flask fitted with a wide glass tube to act as a reflux condenser, and 100 c.c. of sulphuric acid (sp.gr. 1·6) are added. The flask is warmed, gently at first, and then more strongly, until all the metal is in solution. After the solution has cooled somewhat, about 350 c.c. of warm water are added, the liquid is filtered on a pulp pad, and the residue is washed with boiling water. The pad is transferred from the filter to a porcelain crucible, dried, ignited at 900° C. for 1 hour, cooled and weighed.

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* For high-purity metal, annealing is unnecessary.

The weight of residue, multiplied by a factor found as for the mixed acid process (Method B), gives the silicon content of the metal.

COMMENTS.—This method, D, is suitable only for routine analysis. It is considerably more rapid than any of the other methods, as the lengthy heating with acid is avoided, silicon and silica being practically insoluble in sulphuric acid of sp.gr. 1·6.

The work here described was carried out in the Research Laboratories of the British Aluminium Company at Warrington. The author wishes to acknowledge his indebtedness to Dr. A. G. C. Gwyer and to the British Aluminium Company for permission to publish the paper.

Observations on the Use of Adsorption Indicators in Titrations of Halides of Limited or Reversible Ionisation

BY A. J. BERRY, M.A.

IT has been shown by Berry and Durrant (ANALYST, 1930, 55, 613) that phenosafranine* and tartrazine are very satisfactory adsorption indicators for such volumetric determinations involving the use of silver nitrate as have to be carried out in acid solution. Subsequent experiments have amply justified their use, and, although experiments have been made with many other dyestuffs, none has been found to be so good for this purpose, except a pyrazelene, described as *pyrazolone jaune* (Produits chimiques de Saint Denis), which behaved exactly like tartrazine. These indicators may be safely used in the presence of a concentration of free nitric acid of the order of normal. Tartrazine may also be used in the presence of dilute sulphuric acid, but phenosafranine should not be used with this acid, on account of the bleaching action which the acid exerts upon the blue silver derivative of this dyestuff.

No difficulties were encountered in any titrations of halides in which the ionisation was straightforward. When, however, experiments were made with compounds in which the ionisation was known to be limited or reversible, irregularities were to be expected, and were indeed observed. In this connection, two rather different types of limited ionisation have to be considered, *viz.* that of compounds such as chloropentammine cobaltic chloride, $\overset{++}{[\mathrm{ClCo(NH_3)_5}]}\overset{--}{\mathrm{Cl}_2}$, in which two-thirds of the chlorine is ionisable, and that of weak electrolytes, such as the mercuric and thallic halides. In the former, if the co-ordinated complex ion is fairly stable, it is a simple matter to realise the ionisable chlorine by titration with silver nitrate (with phenosafranine as indicator) with a fair degree of accuracy, whereas in the latter the action of the indicator is impeded in such a way as to make the determination of the end-point very difficult, or altogether impossible. The following results may be quoted by way of illustration:

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* Regarding phenosafranine, it should be mentioned that this dyestuff had been used prior to the publication of Berry and Durrant by H. M. Weir (*Dissertation*, München, 1926). The authors were ignorant of Weir's publication, and regret that it was overlooked.

1. (*a*) CHLOROPENTAMMINE COBALTIC CHLORIDE.—Fifty c.c. of a solution of this salt containing 3·22 grms. per litre required 19·45 c.c. of a solution of silver nitrate containing 11·72 grms. per litre, phenosafranine being used as indicator. The percentage of ionisable chlorine is, therefore, 28·9 per cent. To determine the total chlorine, 50 c.c. of this solution were reduced by shaking with a 2·5 per cent. zinc amalgam in presence of very dilute sulphuric acid. The solution required 28·0 c.c. of silver nitrate, with *pyrazolone jaune* as indicator, from which it follows that the total chlorine is 42·7 per cent.

In another experiment the total chlorine was determined by reducing 0·727 grm. of the salt dissolved in 100 c.c. of *N* sulphuric acid by shaking with 2·5 per cent. zinc amalgam. The liquid was then diluted to 250 c.c. with water. Twenty c.c. of silver nitrate (11·72 grms. per litre) required 39·8 c.c. of the reduced cobalt solution, tartrazine being used as indicator. The total chlorine was, therefore, found to be 42·3 per cent. The values calculated from the formula are: 28·3 per cent. for the ionisable chlorine, and 42·5 per cent. for the total chlorine.

Various other experiments were made on this salt, with precisely similar results. It may be noted that phenosafranine is particularly well suited for titrations of the ionisable chlorine, as the end-point is easy to recognise in the presence of the purple-red colour of the solution. The value of liquid amalgams, introduced by Nakazono and Someya for effecting reductions in volumetric analysis, has been amply verified by Russell (*e.g. J. Soc. Chem. Ind.*, 1926, **45**, 57T.), and I have found it to be very convenient for these and for other similar experiments. When a solution of chloropentammine cobaltic chloride is kept for some time, it undergoes slow hydrolysis, with formation of aquopentammine cobaltic chloride, in which all the chlorine is in the ionic condition. This hydrolysis can be followed by titration with silver nitrate, phenosafranine being used as the indicator. It was found that in a solution which had been kept for three weeks at the ordinary temperature, the ionisable chlorine had increased by over 25 per cent.

$$[ClCo\overset{++--}{(NH_3)_5}]Cl_2 + H_2O = [(H_2O)Co\overset{+++---}{(NH_3)_5}]Cl_3.$$

(*b*) CHROMIC CHLORIDE.—It is well known that the three modifications of the hexahydrate of this salt differ not only in colour, but also in their behaviour towards silver ions. In the violet form all the chlorine is in the ionic condition, in the light green form (Bjerrum's salt) this amounts to two-thirds, whilst in the dark green form only one-third of the chlorine is in this condition. The rapidity of the transformations in aqueous solution, however, renders verification of these phenomena by analytical methods exceedingly difficult. The investigations of

Weinland and Koch (*Z. anorg. Chem.*, 1904, 39, 296) and of Olie (*ibid.*, 1907, 52, 48) have shown that the presence of strong acids exerts an impeding action on the transformation of the green salt into the violet isomer, and the following attempt to verify this phenomenon by titration with silver nitrate, with the aid of an adsorption indicator, although only partly successful, may be of interest.

Anhydrous chromic chloride cannot be dissolved directly by water, but traces of reducing agents which produce some chromous chloride enable the salt to dissolve easily (Drucker, *Z. physikal. Chem.*, 1901, 36, 173). After various methods had been tried, it was found most convenient to dissolve the salt by shaking with 2·5 per cent. zinc amalgam and dilute acetic acid. The liquid thus obtained was left exposed to the air for a short time to allow any chromous salt to be reoxidised to the chromic condition. It was then divided into two equal portions, one of which was diluted with four times its volume of water, and the other with four times its volume of normal nitric acid. These solutions were then titrated with silver nitrate (approximately *N*/14), phenosafranine being used as indicator. The solution which had been diluted with water gave very sharp end-points, whereas that which contained nitric acid gave an incipient end-point when less than one-third of the volume of silver nitrate was run in from the burette. When shaken, however, the precipitate changed from blue to pink, and on addition of more silver nitrate, the same volume was ultimately required as in the former case. While valueless from the standpoint of quantitative accuracy, these experiments do give some qualitative verification of the action of hydrogen ions in restraining the transformation of the green univalent $\overset{+}{[Cr(H_2O)_4Cl_2]}$ ion into the violet tervalent $\overset{+++}{[Cr(H_2O)_6]}$ ion.

2. Weak Electrolytes.—That silver chloride is soluble in mercuric nitrate solution was known to Wackenroder, and recognised by Stas as a source of error in the determination of silver in presence of mercuric salts. It was not surprising, therefore, to find that titrations of mercuric chloride by means of silver nitrate with adsorption indicators should be unsuccessful. More unexpected, however, were the highly irregular results which were obtained when thallic halides were titrated in this way with silver nitrate. The thallic halides resemble the mercuric halides to some extent in being weak electrolytes (Berry and Lowry, *J. Chem. Soc.*, 1928, 1748), and also in having a marked tendency to form complex ions. It is particularly to be noted that this is a property of thall*ic* ions, and does not in any way apply to thall*ous* ions. It was found that the end-points with adsorption indicators in titrations with hydrochloric acid and silver nitrate were in no way altered in the presence of considerable quantities of thallous nitrate, in whichever way the titrations were carried out. The disturbing action of thallic ions was demonstrated by numerous experiments, of which the following may be described as the most impressive.

Equal volumes of a solution of silver nitrate (approximately *N*/14) were diluted, in one experiment with an equal volume of *N* nitric acid, and in the other with an equal volume of the same acid containing a small quantity of thallic oxide in solution. These solutions were titrated with *N*/20 hydrochloric acid.

When the silver nitrate solutions were titrated with the hydrochloric acid run in from the burette, with tartrazine as indicator, the quantity of acid required was approximately 20 per cent. *greater* in the solution containing the thallic salt. If the titration was carried out in the reverse direction, with phenosafranine as indicator, the volume of the silver solution required was approximately 21 per cent. *less* in the solution which contained the thallic nitrate than in the other. Moreover, the end-points were indistinct in all the titrations in which thallic nitrate was present. These differences were considerably accentuated when potassium bromide was used instead of hydrochloric acid for the titrations. Further confirmation of these irregularities was obtained in numerous analyses of thallium sesquichloride, $TlCl_3.3TlCl$, a salt which is easy to prepare in a high degree of purity. One further observation on this subject may be quoted: thallic oxide is much more rapidly dissolved by $N/10$ hydrochloric acid than by N nitric acid, thereby showing the tendency of thallic ions to combine with chlorine ions.

In titrations involving the use of adsorption indicators, it is frequently desirable to aid flocculation of the silver halide. This may be easily effected by adding a small quantity of a bivalent electrolyte, such as strontium nitrate, or, better still, of a tervalent electrolyte, such as lanthanum nitrate.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE USE OF ULTRA-VIOLET LIGHT FOR THE DETECTION OF TRACES OF SULPHITES

At the suggestion of Mr. J. A. Radley, we have made a series of experiments on the detection of sulphites by oxidation to sulphuric acid and formation of the fluorescent quinine sulphate.

A boiling-tube was fitted with a tap-funnel, and an outlet consisting of an inverted U-tube with a bulb blown in each leg. This delivered into a test-tube immersed in cold water and containing 5 c.c. of boiled distilled water and 1 c.c. (or less) of the purest hydrogen peroxide (40 vol.) obtainable. About 10 c.c. of a solution containing known amounts of potassium sulphite were measured into the boiling-tube, sufficient 50 per cent. hydrochloric acid to acidify the mixture was added through the tap-funnel, and the whole was boiled gently so as to distil over 2 or 3 c.c. of water. The contents of the test-tube were then shaken well with a speck of quinine and examined in filtered ultra-violet light, when the presence of 0·25 mgrm. or more of sulphur dioxide was indicated by the brilliant violet fluorescence of quinine sulphate.

The only disadvantage of the method is the great sensitiveness of the fluorescence reaction. In the first place, it is extremely difficult to obtain a sample of hydrogen peroxide or of bromine water which does not itself fluoresce with quinine, and, for this reason, the minimum quantity of the former must be used. Secondly, care must be taken that no spray reaches the test-tube during the distillation. Attempts to increase the sensitiveness by adding powdered calcium carbonate to the acid solution, so as to produce a non-oxidising atmosphere of carbon dioxide, were not successful, as a fluorescence was obtained without addition of sulphite. When phosphoric acid was used in place of hydrochloric acid high blanks were again obtained, and it should be noted that quinine phosphate also fluoresces in filtered ultra-violet light. The blank fluorescence obtained under the experimental conditions recommended above is, however, too weak to be confused with that from 0·25 mgrm. of SO_2.

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SANDALWOOD AND ITS SUBSTITUTES

THE two photomicrographs reproduced in the February issue of THE ANALYST (p. 124), representing tangential longitudinal sections of sandalwood and kalamet wood, respectively, do not show with sufficient clearness the structures intended.

Sandalwood (*Santalum album*) Kalamet Wood (*Mansonia Gagei*)

Tangential longitudinal Sections magnified × 50 lin.

The accompanying photomicrographs, taken at a higher magnification (×50), show the storage rays more clearly. It will be seen that the rays (*viz.* the lenticular, porous zones) of kalamet wood (*Mansonia Gagei*) are arranged in tiers, or stories, which appear to the naked eye or when examined with a hand-lens as "ripple marks." These form a feature of specific, diagnostic value in certain woods, and may be seen on polished longitudinal sections as fine parallel lines; the average number per inch is worth recording for any given species.

It should be noted that in true sandalwood (*Santalum album*), on the other hand, the rays possess no such definite arrangement.

In the last line of the original note, "Fig. 3" should read "Fig. 4."

3, RAWLINSON ROAD, OXFORD
J. CECIL MABY

POISONING BY CARBON MONOXIDE FROM A GAS-HEATER

On December 19th, 1931, a man and woman, aged 25 and 49, respectively, were seen about 5 a.m. by the man's brother, who slept in a room leading out of their room. He thought at that time that nothing was wrong, and it was not until 11 a.m. that, on passing through the room a second time, his suspicions were aroused, and he informed the police, and the man and woman, who were unconscious, were taken to a hospital. On both occasions when he passed through the room he had noticed that the man was lying in bed and that the woman was in a sitting position on the floor. The woman died after a known period of unconsciousness of about 24 hours. The man recovered after a period of unconsciousness of about 36 hours. The former was deeply unconscious all the time, but in the latter unconsciousness was light.

Clinically, except for slight cyanosis, dilated but reacting pupils, an irregular feeble pulse, and the fact that the man had vomited prior to admission, there was no evidence of poisoning, but the taking of a narcotic poison was presumed.

The post-mortem findings in the case of the woman were quite negative, as was also the analysis of the viscera. The blood of the woman contained no carbon monoxide. No poison was detected in the vomit of the man. A small bottle of tablets of two kinds (aspirin and potassium chlorate) was found in the room.

The man, on recovery, denied that there was a suicide pact, or that he had taken poison. He could not account in any way for what had happened, and remembered nothing after getting into bed. He was living, he said, happily, and was in regular work.

In view of the negative findings, an enquiry was made about coal-gas poisoning. The brother who had passed through the room had smelt nothing, and the police found the gas-taps in order, and the gas-meter was of a quarterly variety. When the police arrived, a small gas-stove was burning in the room; it was subsequently elicited that the occupants of the room were not in the habit of leaving the stove burning all night. At this time, some six weeks after the tragedy, I requested that the gas-stove should be sent to me. It had been sold, and, after some difficulty, was found by the police in a second-hand dealer's shop, and was sent to me. I further elicited the fact that it was not connected with the chimney in the room, and that the regulator of the chimney was closed, so that all fumes from the burning stove must have been discharged into the room. The gas-stove was of a very old-fashioned pattern, and one which might be expected to produce carbon monoxide.

The room occupied by these persons was 13 ft. 3 in. by 11 ft. 4 in. by 8 ft. It had two doors, one of which was closed and the other open to the width of a crack, and one window, which was closed, except for a quarter of an inch at the top. The bed was between the stove and the door leading to the second room, which was also the one open the width of a crack. The man was found lying on the side of the bed nearer to the slightly open door, and the woman was found on the floor on the opposite side of the bed, *i.e.* away from the slightly open door.

I arranged for the stove to be sent to the Government Chemist, and his report, based on work done by Mr. L. C. Nickolls, of that department, is most interesting, and is here given in detail.

REPORT OF THE GOVERNMENT CHEMIST.—"The gas-heater has been tested under varying conditions of gas consumption and air supply.

"When the heater is burning its maximum quantity of from 10 to 12 cubic feet of gas per hour, the amount of carbon monoxide in the products of combustion is approximately 2 parts in 10,000, equivalent to 20 parts in 10,000 of the gas burned, and the equilibrium concentration in the air of the room (13 ft. 3 in. × 11 ft. 4 in. × 8 ft. = 1200 cb. ft.) is:

Assuming:	½ air-change per hour	1 air-change per hour	2 air-changes per hour
	0·5	0·25	0·1 part in 10,000

"These concentrations of carbon monoxide are innocuous. Similarly, when the gas supply to the heater is reduced to 5 cubic feet an hour, no increase in the quantity of carbon monoxide produced is observed. When, however, the gas supply is maintained at about 8 cubic feet per hour, a critical condition exists in the behaviour of the heater, and, irrespective of alterations in the air supply, relatively very large quantities of carbon monoxide are produced, and dangerous concentrations in the air of the room might be obtained.

"In one experiment the exit gases from the heater contained 71 parts in 10,000 of carbon monoxide (equivalent to 1780 parts in 10,000 of the gas burned), and the equilibrium concentration in the above room would be:

Assuming:	½ air-change per hour	1 air-change per hour	2 air-changes per hour
	24	12	6 parts in 10,000

"The two former concentrations are lethal, the last after some hours' exposure might prove lethal.

"The probable number of air changes an hour in the room in question is based upon the following considerations:—In the first report of the Departmental Committee to enquire into the ventilation of factories and workshops, 1902 (Appendix II, p. 105), it is stated that in small rooms having all apertures closed the ventilation varies from ½ to 2 air-changes an hour, while the Director of the Building Research Station, Department of Scientific and Industrial Research, has reported that the air-changes in a closed room may vary from ½ to 1½ an hour."

Effect of Carbon Monoxide.—If about one-half of the blood is unavailable for carrying oxygen (*i.e.* 50 per cent. saturation with carbon monoxide), the patient will be seriously ill, but, if removed from the vitiated atmosphere, will recover in many instances. If, however, such a saturation is maintained in his blood for a period of hours, it follows that during this time sufficient oxygen is not reaching the body, particularly the brain, with the result that the latter becomes damaged. Although the patient when removed from the vitiated atmosphere rids himself of the carbon monoxide, the damage which has already taken place to the brain-cells is such that unconsciousness persists, and the patient may die. This distinction is important, as the person who puts his head in a gas-oven, for example, and dies in a few minutes, dies directly from the effects of poisoning by carbon monoxide.

Evidence of Carbon Monoxide Poisoning on Arrival of the Patients at the Hospital.—According to the times given to me, about two hours elapsed between the calling of the police and the arrival at the hospital. As soon as patients are removed from the influence of carbon monoxide by ventilation of the room or by being taken into the open air, the concentration of carbon monoxide in the blood rapidly diminishes, and, no doubt, when the patients arrived at the hospital, there was no clinical evidence of poisoning. It is stated that carbon monoxide can disappear from the blood in 30 minutes in fresh air.

Long Period of Unconsciousness in Hospital.—In rapidly fatal cases of carbon monoxide poisoning, death is due directly to the gas. In the cases in question, saturation was slow and never reached a very high level, but exposure was of considerable length. Death was probably due to damage to the brain cells from this long exposure. In the case of the man the damage was less serious, so recovery ensued.

Recovery of the Man and Death of the Woman.—The position of the man in bed, that is to say, nearer the slightly open door, suggests that some ventilation in the form of incoming currents of air resulted in his receiving a lower concentration of carbon monoxide in the air that he breathed, so that the percentage saturation in his blood was less. This is supported by the fact that when the police found him he was not fully unconscious. The position of the woman was very characteristic ("the woman, herself, being in a sitting position on the floor"). No doubt she realised at some time during the night that the stove was still burning, and attempted to get out of bed to extinguish it. When persons are partly under the influence of carbon monoxide, the slightest muscular effort, *e.g.* getting out of bed, is accompanied by great breathlessness, resulting in the inhaling of still more carbon monoxide, and great muscular weakness. As soon as she got out of bed, she immediately collapsed on the floor, and found herself unable to move. As she was well away from the window and the door, the concentration of carbon monoxide reached a higher level in her blood than in that of the man, so that, when found, she was fully unconscious, and during the time which elapsed between the gassing and the giving of the alarm, the percentage saturation in her blood was maintained at a sufficiently high level to produce ultimately a fatal result.

History of the Exposure.—Assuming that the stove was lit about midnight, and that the patients were first seen about 5 to 6 a.m., there had been from 5 to 6 hours' exposure. The brother then walked through the room and, no doubt, caused some temporary ventilation. The two persons were then exposed for another 5 hours. As the concentration in the room for the first few hours that the stove was burning would be very low, it may be assumed that they had about 7 hours of effective exposure to a noxious concentration of carbon monoxide in the air of the room.

When the blood is about 25 per cent. saturated with carbon monoxide, the first symptoms appear; at 30 to 35 per cent. definite symptoms, such as increased breathing, muscular weakness, giddiness, etc., occur; at 50 per cent. the symptoms become urgent; at 50 to 60 per cent. unconsciousness supervenes; and at 65 to 85 per cent. death will occur. In the case of the man, the highest percentage reached in the blood was probably about 50 per cent., and for the woman the percentage was rather higher. Breathing 15 to 20 parts of carbon monoxide in the air per 10,000 parts can cause death in 4 hours and upwards, that is to say, at 65 to 85 per cent. saturation. In these cases I suggested that about 50 per cent. saturation occurred, and that it was maintained for about 7 hours. Therefore, it is fair to assume that the concentration in the air of the room was, for most of the time, considerably less than 15 parts per 10,000 of carbon monoxide. From the report of the Government Chemist, it is evident that, even with 1 air-change per hour, the concentrations I postulated in the blood of these people could easily have been attained.

G. ROCHE LYNCH

DEPARTMENT OF CHEMICAL PATHOLOGY,
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LONDON, W.1

Official Appointments

THE Minister of Health has approved the appointment of:

JAMES THOMPSON, Ph.D., F.I.C., as Public Analyst for the County of Berkshire, in place of Sir W. R. Smith (deceased).

The appointment of ALAN WEST STEWART as Additional Analyst terminates on the appointment of James Thompson as successor to the late Sir W. R. Smith (June 15th, 1932).

ALAN WEST STEWART, D.Sc., F.I.C., as Public Analyst for the Metropolitan Borough of Paddington (June 22nd, 1932).

The Minister of Agriculture and Fisheries has confirmed the following appointments:

HAROLD LOWE, M.Sc., F.I.C., previously Deputy Agricultural Analyst, now appointed Agricultural Analyst for the County of Denbigh, vice W. F. Lowe (deceased).

J. AUGUSTUS VOELCKER, C.I.E., M.A., Ph.D., F.I.C., as Agricultural Analyst for the County Borough of Oxford, vice Sir W. R. Smith (deceased).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE FIRST QUARTER, 1932

OF the 1285 samples examined under the Food and Drugs Act during the quarter, 110 were formal and 1175 informal; 83 were adulterated or incorrect. Seventy-one of the 668 samples of milk were condemned.

LABELLING OF JAM.—Three informal samples of jam had the name of the jam on the label in very large type and the words "with other fruit juice" in very small type. The Food Manufacturers' Federation was informed of the conditions on which manufacturers are allowed to use the Federation label.

GREY POWDER TABLETS.—These were half-grain tablets and should have contained one-sixth of a grain of mercury and one-third of a grain of chalk in each tablet. In this sample the mercury was 20 per cent. deficient. The vendor was communicated with, and later a letter was received from the wholesale dealers supplying him, stating that the deficiency was probably due to the fact that the tablets had been in stock about four and a half years. Experiments made by them had established the fact that loss of mercury occurred if grey powder tablets were kept in stock for too long a period.

This explanation is quite reasonable, since mercury is volatile even at temperatures below freezing-point. The vendor was warned that grey powder tablets should not be kept in stock for a longer period than six months, in which time the loss of mercury would probably be less than 5 per cent.

H. H. BAGNALL

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

"HONEY AND BUTTER ROCK" WITHOUT HONEY

On June 14th a Plymouth firm of wholesale sweet manufacturers was summoned at Camborne, Cornwall, for selling at Redruth, on February 13th, honey and butter rock bearing a false label. Originally the Cornwall County Council had proceeded against a firm of grocers, and when the case was dismissed after the production of a warranty, a summons had been issued against the wholesalers.

Mr. W. W. Johnston, for the County Council, said that the jar containing the sweets stated that they were guaranteed to be pure and to comply with the Food and Drugs Act. The Public Analyst (Dr. H. E. Cox) had certified that the rock consisted of cane sugar with a little butter, but contained no honey.

For the defence, it was contended that the rock had to be boiled at a high temperature, and that if a lot of butter and honey were put in, the sweets would lose their real properties. The defendants had realised all along that the label was misleading. There was no necessity for them to alter the sweets, but there would be a new label which would comply completely with the Act.

The Bench imposed a fine of £5.

Department of Scientific and Industrial Research

FOOD INVESTIGATION

THE YELLOWING OF THE ABDOMINAL FAT OF FROZEN RABBITS*

If the fatty tissues of the wild rabbit (*Lepus cuniculus*) are stored at temperatures below the freezing-point of water, the exposed surfaces frequently acquire a pronounced yellow colour, which may even deepen to orange, and is accompanied by a sharp odour resembling that of "blown" linseed oil. An apparently similar type of yellowing occurs on certain slowly frozen fish. The period between the killing of rabbits in Australia and marketing in this country varies considerably, probably averaging 4 to 5 months. The temperature at which they are held during the voyage probably averages about −10° C. Experiments, having in view a study of the pre-freezing treatment, and temperature and duration of storage, were carried out in England on trapped rabbits. The fat is semi-liquid at body temperature, and is still soft at −10° C.; and films exposed to the air set slowly with moderately tenacious skins. The fat is highly unsaturated, the iodine values for those used in this work varying from 119 to 179. To determine the degree of yellowing, the yellow fraction was separated from the total fatty acids. The dissected yellow fat was ground with sand, dried over anhydrous sodium sulphate, treated with alcohol until no further colour was extracted, the alcohol was evaporated, and 2 to 3 grms. of the fatty acids were treated with 100 c.c. of petroleum spirit. The yellow fraction was precipitated on the walls of the vessel, and cooling for several hours at about +5° C. was necessary to complete separation. The precipitated fraction was washed with petroleum spirit, most of the solvent was removed, and the fraction was dissolved in hot absolute alcohol. This was removed and the fraction was weighed. Attempts to estimate the degree of yellowing were also made, but colorimetric comparisons of the fats were not practicable, owing to the insolubility of the deeply-coloured fats in all solvents but hot alcohol. Statistical comparisons, however, were made by examination at definite intervals. The storage experiments showed that yellowness could be produced in the fat by storing the rabbits for a sufficient time in the frozen condition, the yellowness becoming more pronounced as storage proceeded; the standards of colour adopted were pale yellow, dark yellow, orange, and dark orange. The difficulty of allowing for the varying amounts of adipose tissue was found not to be serious. After the initial latent period, intensity and depth of penetration of the yellowness were found to be approximately proportional to the duration of storage at a given temperature, being greater the higher the temperature. The duration and temperature of storage in the pre-freezing period are responsible for the rapidity of yellowing, storage for two days at atmospheric temperature subsequently enhancing yellowing to approximately the same degree as one month's storage at —5° C. At —18° C., yellowing is, commercially, almost prevented, and the duration of storage sufficient to affect the market value of rabbits kept at —10·5° C., varied from 3 to 5 months according to the pre-freezing treatment used. The investigation of the causes of yellowing included a study of the effect of micro-organisms, but these were definitely excluded as a cause of the phenomenon. The evidence for this particular type of oxidation by atmospheric oxygen as the cause of pigmentation is largely circumstantial, but the possibility of the liberation of an enzyme which catalyses the yellowing process in the fat cells during freezing is regarded as possible. Further, the presence of water and blood (haemoglobin) was found to exert a marked accelerating influence on the process. The yellow fraction is regarded as originating in the oxidation of the linoleate glycerides in the presence of an oxidase with or without water and haemoglobin in the fatty tissues, and the pigment itself is probably an unsaturated ketonic compound. It may be that the rate of yellowing in fats stored at a fixed temperature is greater the lower their initial iodine values. The necessity for storing the carcases in the frozen condition for as short a period as possible, in both the exporting and importing countries, is emphasised, and, so far as is possible, the temperature of storage should be not higher than —14° C.

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* Special Report No. 42, by J. R. Vickery. Obtainable at Adastral House, Kingsway, W.C.2. Price 6d. net.

D. G. H.

International Vitamin Standards

IN June of last year, under the auspices of the Permanent Commission on Biological Standardisation of the Health Organisation of the League of Nations, a Conference of experts was held in London with the object of discussing the possibility of adopting standards and defining units for certain of the vitamins. As a result of their deliberations the Conference made a series of important recommendations to the Permanent Standards Commission, and these are set out in the Report [No. C.H. 1055 (1)],* Briefly, the Conference recommended the adoption of a standard, and the definition of a unit in terms of such standard, for the four vitamins *A*, B_1, *C* and *D*. The Conference further recommended that in the case of the two vitamins, *A* and *D*, the final preparation of the standard should be undertaken by the National Institute for Medical Research, Hampstead, and that the standard for vitamin B_1 should be prepared in Java. The

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* Obtainable from Messrs. Allen & Unwin, 40 Museum Street, W.C.1

National Institute at Hampstead was further nominated to act, on behalf of the Health Organisation of the League of Nations, as the central laboratory for the storage and distribution of the three standard preparations for vitamins *A*, B_1 and *D*. In the case of vitamins *A*, *C* and *D*, it was recommended that the proposed standards and units should be adopted for a period of two years in the first instance, the standard for vitamin B_1 being given a preliminary currency of five years. In the case of vitamin *C* no preparation or storage of a stable standard was involved by the recommendation of the Conference which was satisfied, for this vitamin, to recommend the use of fresh lemon juice as a standard, and to define the unit as the anti-scorbutic activity of 0·1 c.c. of the juice, prepared according to a simple method described in the Report.

VITAMIN *A*.—Carotene was recommended as the international standard for vitamin *A*, and the unit was defined as the vitamin *A* activity of 1γ (0·001 mgrm.) of the standard preparation of carotene. Eight laboratories have contributed varying quantities of carotene, and these have been mixed at the National Institute for Medical Research; the mixed carotene has been purified by recrystallisation until the melting point is above 179° C. The highly purified preparation has been distributed in 10-mgrm. quantities into small ampoules in an atmosphere of pure nitrogen, reduced to dryness, and the ampoules sealed.

VITAMIN *D*.—With regard to the international standard for vitamin *D*, the Conference recommended that the standard solution of irradiated ergosterol, which has been issued from the National Institute for Medical Research, Hampstead, for the past two years (*cf.* ANALYST, 1930, **55**, 692; 1932, 174), should be adopted as the international standard. On account of the fact that this standard preparation had been intended, primarily, for the needs of this country alone, it was considered desirable to prepare a larger quantity to meet the needs of other interested countries—19 in all—for a period of some years. Accordingly, a second and larger quantity of irradiated ergosterol has been prepared at the National Institute for Medical Research, and this has been assayed in terms of the original standard preparation. The comparative examination of the new and the original standard preparations has been carried out by eight different laboratories in five different countries, and these eight groups of workers are unanimous in agreeing that the new standard now available is exactly equivalent to the original standard. There is, accordingly, now available an adequate amount of this standard preparation of vitamin *D* to meet the requirements of all workers throughout the world for some years to come. The unit recommended for international use is defined as the vitamin *D* activity of 1 mgrm. of the international standard solution of irradiated ergosterol.

VITAMIN B_1.—The standard for vitamin B_1 recommended for international adoption is a concentrated preparation of the anti-neuritic vitamin B_1, adsorbed on kaolin. The standard has been prepared in the Medical Laboratory, Batavia, Java, and is stored at the National Institute for Medical Research, Hampstead, from which it will be distributed. The international unit has been defined as the anti-neuritic activity of 10 mgrms. of the international standard preparation. The standard preparation is very stable, and, provided it is protected from moisture, appears to retain its activity unchanged.

In the case of other countries, arrangements have been made to send suitable supplies of each of the above standards to approved national institutions for local distribution. Institutions or individual investigators in Great Britain and Ireland, who wish to obtain supplies of one or more of these standards, should apply to the Department of Biological Standards, National Institute for Medical Research, N.W.3, from which issues will be made at regular intervals.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Composition of Shell Eggs. L. C. Mitchell. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 310–326.)—The methods used for determining total solids, chlorine, phosphorus, organic and ammoniacal nitrogen, and dextrose, are those described in *Methods of Analysis* (*A.O.A.C.*), 1930, 244–249. Crude albumin nitrogen is taken to be the water-soluble nitrogen precipitable by 40 per cent. alcohol. The fat was determined by hydrolysis as follows:—Approximately 2 grms. of yolks, or 3 grms. of whole eggs, or 5 grms. of whites, are weighed accurately by difference from the well-mixed sample into a Mojonnier fat-extraction tube, 10 c.c. of concentrated hydrochloric acid being then added slowly and with vigorous shaking. The tube is placed in a water-bath at 70° C., this being then brought to the boiling point and kept boiling for 30 minutes, during which time the tube is carefully shaken at five-minute intervals. The tube is afterwards removed from the bath, and, after addition of water (better than alcohol) to fill the lower bulb of the tube, cooled to room temperature. The contents of the tube are next mixed, first with 25 c.c. of ether and then with 25 c.c. of redistilled petroleum spirit (b.pt. below 60° C.), and allowed to stand until the ethereal layer becomes clear. This layer is decanted into a weighed 125-c.c. beaker-flask containing two or three porcelain chips, the solvent being evaporated slowly on a water-bath. The residual liquid is subjected to two further extractions, 15 c.c. of each of the two solvents being used each time and mixed in separately as before. The clear solvent layer is again decanted into the beaker-flask, and the residue left on evaporation of the solvent is dried at 100° C. to minimum weight. The vessel is then left in the air until it no longer changes in weight. The weight of the residue thus obtained is corrected by a blank determination on the reagents.

Numerous data, referring to two-day-old eggs, commercial fresh eggs, and storage eggs separately, are given. The outstanding feature of the results is the uniformity in composition shown by fresh eggs. Certain changes in composition with increasing age of the egg are indicated, and further work in this direction will be reported later. Both whites and yolks separated from fresh and storage eggs exhibit differences in composition which indicate osmotic action, and suggest a possible means of ascertaining the freshness of eggs. T. H. P.

Decomposition of Lecithin in Eggs. L. C. Mitchell. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 282–284.)—A sample of whole eggs, broken under presumably aseptic conditions just before being sent by post to various analysts, gave percentages of lipoid phosphorus (as P_2O_5), varying from 0·37 to 0·08. The control sample was divided into a number of portions, which were analysed from time to time until they became putrid. With some of these portions, which exhibited normal putridity, the proportion of lipoid and of phosphoric anhydride in the lipoid suffered little change. With others, which developed a creamy colour and a pasty consistence, the percentage of lipoid diminished slightly, and that of phosphoric anhydride in the lipoid enormously; the nitrogen also decreased markedly, and the acidity showed a large increase. For the lipoids of two of the portions the following results were obtained:

	Lipoid present Per Cent.	Phosphoric anhydride Per Cent.	Nitrogen Per Cent.	Acidity in c.c. of C_2H_5ONa per grm.
Putridity normal	12·68	2·67	0·55	4·0
Putridity abnormal	11·54	0·17	0·16	60·0

The decomposition of lipoid material occurring in the abnormal cases evidently involves a breakdown of the lecithin, with formation of fatty acid and disappearance of lipoid phosphorus and choline nitrogen. That this change is due to bacterial growth is shown by the observation that inoculation of fresh eggs with the abnormal eggs induces similar changes. The bacteria apparently produce the enzyme lecithinase, which attacks lecithin. T. H. P.

Determination of Nitrogen in Yeast by the Hydrogenation Method. H. ter Meulen and K. Peeren. (*J. Inst. Brewing*, 1932, **38**, 330–331.)—As a result of the erratic results obtained by Thorne (*id.*, 1932, **38**, 28), further details of ter Meulen's method (*Rec. Trav. Chim. Pays-Bas*, 1924, **43**, 643; 1930, **49**, 396) are given. One c.c. of a 1 per cent. suspension of the sample in water is mixed with 0·5 grm. of nickel formate in a porcelain boat, and the mixture is then dried and heated in a current of hydrogen at 250° C., the gases being passed through 10 grms. of soda-lime (to trap any unchanged formic acid) and nickel-asbestos. The resulting ammonia is titrated with 0·01 *N* acid from a burette reading to 0·001 c.c. The determination takes 30 minutes, and the values for 10 samples of brewer's or baker's yeast, which were accurate to within about 0·002 mgrm., confirm the previous results, namely, that the method gives results from 0·8 to 19·1 per cent. higher than those obtained by the Kjeldahl–Gunning method, these differences being, on the whole, greater than those between the Gunning and Christensen–Fulmer modifications.

ABSTRACTOR'S NOTE.—It has been found that the most suitable apparatus for this method is a resistance-glass tube about 40 cm. long and 2 cm. in diameter, passed through holes in the ends of an asbestos or tin box 25 cm. long. The portion of the tube inside the box is packed with a catalyst consisting of an intimate mixture of asbestos and reduced nickel prepared by heating black nickel oxide in hydrogen at 320° C. Soda-lime is also required if halogens or sulphur are present. Nickel formate is prepared by the action of formic acid on precipitated nickel carbonate, and if 0·1 grm. is mixed with 0·05 grm. of sample and 0·5 grm. of reduced nickel, reduction is greatly facilitated. A blank determination should first be made to ensure that the apparatus is free from nitrogen, and the boat containing the sample is then inserted in the portion of the tube outside the box and heated in a current of hydrogen, gently at first, and, finally, to a red heat, the portion of the tube inside the box being maintained at 250 to 300° C. (inside temperature). J. G.

Volumetric Method for the Determination of Formic Acid in Fruit Juices and Fruit Syrups. G. v. Szelényi. (*Z. Unters. Lebensm.*, 1932, **63**, 534–541.)—In Fincke's method (*id.*, 1911, **21**, 1; **22**, 88; ANALYST, 1911, **36**, 103, 496) such quantity of reaction mixture should be chosen that at least 0·01 per cent. of mercuric chloride (added in the form of a solution containing 100 grms. of mercuric chloride and 30 grms. of sodium chloride per litre) is present. Preferable methods are as follows:—(1) The sample is subjected to preliminary treatment, as in Fincke's method, and a portion of the filtered distillate, corresponding with 10 to 30 c.c. of juice or 30 grms. of syrup, is mixed in a stoppered flask with 5 c.c. of a 10 per cent. solution of sodium acetate and 15 to 20 c.c. (*x* c.c.) of 0·1 *N* bromoacetic acid, the extent of the decolorisation being an indication of the amount of formic acid present ($HCOOH + Br_2 = CO_2 + 2HBr$). After 30 minutes 5 c.c. of a 10 per cent. solution of potassium iodide are added, and the mixture is titrated with 0·1 *N* sodium thiosulphate solution (*y* c.c.). Then $2{\cdot}3(x - y)$ gives the formic acid in mgrms. (allowance being made for any blank), with an error of 0·05 to 0·5 mgrm., whilst Fincke's method gives lower results. Blank tests with samples of raspberry juice and syrup free from formic acid yielded 0·5 per cent. (on 10 c.c.) and 1 to 1·5 per cent. (on 30 grms.), respectively, the corresponding figures obtained by Fincke's method being appreciably higher. (2) Calcium formate is produced by the addition of calcium carbonate (*cf.* Fincke, *loc. cit.*), and 200 to 300 c.c. of the mixture are heated with 10 c.c. of 10 per cent. sodium carbonate solution, 20 c.c. of 0·1 *N* potassium permanganate solution being then added rapidly, followed, after 1 minute, by 1 or 2 c.c. of a 10 per cent. solution of zinc sulphate. This removes any colloidal manganese compounds and sharpens the end-point of the final titration, which is carried out with 0·1 *N* arsenic acid. Then 1 c.c. of 0·1 *N* potassium permanganate solution ≡ 2·3 mgrms. of formic acid (*cf.* Hanak and Kürschner, ANALYST, 1931, **56**, 116) is added. If 45 minutes are allowed for the oxidation stage, the procedure may be carried out in the cold, and the results, though slightly higher, have an error of only 0·02 to 0·3 mgrm., and, again, are more accurate than those obtained by Fincke's method. Method (2) is better for fruit juices than for syrups, as the latter give higher blanks and develop a yellow colour due to decomposition products of the sugars. J. G.

Aluminium in the Ash of Plant Materials, Fruit Juices, and Similar Products. L. Hart. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 285–289.)—With the accepted methods based on the initial precipitation of iron and aluminium as phosphates, if the aluminium is calculated by difference after the iron and phosphoric acid have been determined, the result is subject to the errors of such determinations, whilst the colorimetric method with aluminon (ammonium aurin-tricarboxylate) requires very small amounts (less than 0·1 mgrm.) of aluminium in the comparison solutions. In the method now proposed, aluminium and iron are separated at *p*H 4 as phosphates, which are then dissolved in acid; the iron is removed by means of cupferron, and the aluminium is precipitated with 8-hydroxyquinoline. The method has been developed primarily to determine aluminium in apple vinegar, and gives good results with a synthetic mixture having the composition of apple ash.

The reagents used are: (*a*) 0·04 per cent. solution of bromocresol green in alcohol; (*b*) 5 per cent. ammonium nitrate solution adjusted to *p*H 4 with acetic acid [yellow-green with (*a*)]; (*c*) 6 per cent. aqueous cupferron solution; (*d*) 2·5 per cent. 8-hydroxyquinoline solution, prepared by triturating 2·5 grms. of the reagent and 5 c.c. of glacial acetic acid, pouring into water at 60° C., cooling, filtering, and diluting to 100 c.c.; (*e*) aluminium-free ammonia, prepared by distilling ammonia solution into water until the resulting solution is at least of 20 *N* concentration; to be kept in a bottle lined with paraffin wax or ceresin; (*f*) 5 per cent. ammonia solution. A quantity of the substance containing 2 to 10 mgrms. of aluminium is ashed at a red heat in an electric muffle until carbon-free, the ash being moistened, dried and again heated, if necessary. The ash is dissolved in dilute hydrochloric acid (1 + 4), and any iron is oxidised with a few drops of nitric acid. Any residue is filtered off, ignited, fused with sodium and potassium carbonates, and dissolved in a little hydrochloric acid (1 + 4), the solution being added to the filtrate. Unless a fivefold excess of P_2O_5 over the equivalent of iron and aluminium is assured, 0·1 grm. of monopotassium phosphate is added. After addition of 1 to 2 c.c. of (*a*) and 10 c.c. of ammonium acetate solution the liquid is partly neutralised with redistilled ammonia, and treated gradually, while gently boiling, with ammonium acetate solution until it assumes a yellow-green colour. It is boiled gently for 1 to 2 minutes to coagulate the precipitate, which is allowed to settle, filtered off on a 7 cm. Whatman No. 41 filter paper, washed two or three times with the cold ammonium nitrate solution, and transferred to the original beaker. The filter is washed into the beaker with hydrochloric acid, and then with hot water, the ferric and aluminium phosphates being dissolved, by heating if necessary. A few crystals of potassium monophosphate are added and re-precipitation at *p*H 4, as above, is effected. The precipitate is filtered off, washed two or three times with cold ammonium nitrate solution and transferred to a 150-c.c. Pyrex beaker, the residue being dissolved in a known quantity (not over 50 c.c.) of sulphuric acid (1 + 4). The percentage of sulphuric acid in the whole liquid (not above 100 c.c.) is adjusted to 10 to 12, the solution being treated at 10° C., and with gentle stirring, with a slight excess of fresh cupferron solution—formation of a white precipitate, which immediately redissolves, indicates excess. After settling for 2 or 3 minutes, the precipitate is collected, by means of gentle suction, on filter-paper supported by a platinum cone or in a Gooch crucible; the filtrate is caught in a 250-c.c. Pyrex beaker containing cupferron solution to indicate if precipitation is complete, and the precipitate is washed with cold 10 per cent. sulphuric acid containing 1·5 grm. of cupferron per litre. The filtrate is concentrated to about 50 c.c. on the steam-bath, and then evaporated with 10 c.c. of concentrated nitric acid until dense fumes appear. If the solution is not colourless it must be heated with a little more of the acid. The cold liquid is diluted to about 60 c.c. and filtered to remove silica, the filtrate being treated with a slight excess of 8-hydroxyquinoline (1 c.c. of the 2·5 per cent. solution ≡ 1·54 mgrm. of Al), and then with redistilled ammonia until precipitation occurs, a 5 c.c. excess of the ammonia being added. The liquid is digested at 60° to 70° C., until the precipitate coagulates, cooled in ice-water, and filtered through a tared Gooch crucible. The aluminium quinolate precipitate is washed with 5 per cent. ammonia containing a few drops of 8-hydroxyquinoline solution, and dried, at 110° C., to constant weight; it contains 5·87 per cent. of aluminium or 11·10 per cent. of aluminium oxide. A blank experiment on the reagents, together with about 0·01 grm. of iron as ferric salt, should not give more than 0·2 or 0·3 mgrm. of aluminium. If the iron is to be determined, the cupferron precipitate is washed with 10 per cent. ammonia solution, which converts it into ferric hydroxide. If a cloudiness is produced, a second filtration becomes necessary. T. H. P.

Determination of Starch in Feeding Stuffs. G. S. Fraps. (*J. Assoc. Off. Agric. Chem.*, 1932, 15, 304–307.)—The use of taka-diastase in the determination of starch in feeding stuffs is preferable to that of malt, as the correction for the sugars dissolved is smaller. By the official method of acid hydrolysis large amounts of pentosans are included, but the use of weaker acid (0·02 *N*) reduces the quantity of pentosans dissolved, and thereby increases the accuracy of the method. Correction may be made for the pentosans either by determining these or by applying a factor, the value of which is dependent on the nature of the material analysed. Since 1 part of dextrose corresponds with 0·9 part of starch, and 1 part of pentose with 0·8799 part of pentosan, sufficiently exact results are obtained by subtracting the percentage of pentosan from that found for starch. As the proportions of the various pentose sugars produced by the hydrolysis of the pentosans are not known, the exact figures to be used for the reducing factors for copper and for conversion to pentosans are also unknown, but errors thus introduced are small if the percentage of pentosans dissolved by the acid is small. When the results are corrected, hydrolysis with 0·02 *N* acid gives approximately the same results for starch as that with either malt-diastase or taka-diastase.

The procedure recommended is as follows: 2·25 grms. of the material are extracted on a hardened filter paper with five successive 10-c.c. portions of ether, and are then washed, first with 150 c.c. of 10 per cent. alcohol solution, and afterwards with a little strong alcohol, and allowed to become nearly dry. The residue is transferred, with exactly 200 c.c. of water, to a crude fibre beaker. The mixture is heated to boiling point, treated with 20 c.c. of 0·2 *N* hydrochloric acid, boiled for 30 minutes, and filtered through asbestos into a flask; the residue is washed two or three times with hot water into the same flask, the total volume of liquid obtained being 300 c.c. The solution, mixed with 30 c.c. of hydrochloric acid (sp.gr. 1·125), is heated for 2½ hours in a boiling water-bath, cooled, and made up to 500 c.c. On 20 or 40 c.c., neutralised with sodium carbonate, the sugars are determined by the Munson and Walker method. To determine the pentosans, 150 c.c. of the 500 c.c. of solution are distilled with 65 c.c. (measured with a pipette) of concentrated hydrochloric acid in the usual way. T. H. P.

Fatty Acids Associated with Cassava Starch. L. Lehrman. (*J. Amer. Chem. Soc.*, 1932, **54**, 2527–2530.)—Fat was removed from cassava starch by extraction with petroleum spirit, and the residue left on evaporation of the solvent was hydrolysed with hydrochloric acid. The resulting 0·1 per cent. of yellow semi-solid oil (iodine value 78·8) was removed by filtration, and the filtrate was tested for glycerol, with negative results. The unsaturated fatty acids were separated from the saturated fatty acids by the magnesium soap and alcohol method; the latter were identified by their neutralisation values, and the former by oxidation with an alkaline solution of potassium permanganate and extraction of the oxidation-products with chloroform, and then with hot water. Analysis of the resulting hydroxy-stearic acids showed that the original fatty acids contained palmitic, oleic and linolic acids. Bromination of a solution of the unsaturated fatty acids in cold anhydrous ether, and extraction of the resulting white precipitate (after being washed with cold ether and dried) with hot petroleum spirit, yielded hexabromostearic acid (m.pt. 80 to 81° C.), indicating the presence of linolenic acid; attempts to find hexahydroxystearic acid in the oxidation products (*vide supra*) were unsuccessful. The portion soluble in petroleum spirit was found to consist of tetrabromostearic acid, and this confirmed the presence of linolic acid, which was also indicated by the production of tetrahydroxystearic acid on oxidation. Tests for nitrogen, sulphur, phosphorus, halogens, and unsaponifiable matter in the fatty acids gave negative results.

J. G.

Determination of Reducing Sugars by Colorimetric Determination of Unreduced Copper. E. M. Emmert. (*J. Assoc. Off. Agric. Chem.*, **1932, 15,** 327–329.)—The method described results in considerable saving of time when compared with methods in which the cuprous oxide formed is separated quantitatively. The reagents required are as follows: (*a*) A solution containing 40 grms. of copper sulphate per litre; (*b*) a solution containing 200 grms. of Rochelle salt and 150 grms. of sodium hydroxide per litre; (*c*) a solution containing 0·25 grm. of pure dextrose per litre; (*d*) 20 per cent. (by vol.) ammonia solution.

To standardise the copper solution, 10 c.c. of (*c*), 5 c.c. of (*a*), and 5 c.c. of (*b*), in a 150 c.c.-Erlenmeyer flask, are heated to boiling on an asbestos gauze and boiled gently for exactly 3 minutes. The hot liquid is made up to 25 c.c. in a measuring flask, and then filtered as rapidly as possible through any ordinary filter paper able to retain the cuprous oxide, which is discarded. Exactly 5 c.c. of the filtrate are made up to 50 c.c. with reagent (*d*) in a measuring flask. The blue colour of this solution is compared with that produced by 5 c.c. of reagent (*a*) when subjected to the same procedure, except that the 10 c.c. of dextrose solution is replaced by 10 c.c. of water. The number of mgrms. (X) of dextrose equivalent to 5 c.c. of the copper sulphate solution is calculated from the formula: $X - XR/U = Y$, in which U is the colorimetric reading of reagent (*a*) without added dextrose, R the reading after reduction with dextrose, and Y the number of mgrms. of dextrose added. This standardisation should be made in duplicate or triplicate.

The approximate sugar content of the solution to be analysed is determined by boiling 10 c.c.-portions of it with different quantities of the mixture of copper sulphate and alkaline tartrate solutions. The sugar solution, if necessary, is diluted or evaporated until 10 c.c. contains from 5 to 20 mgrms. of reducing sugar, expressed as dextrose. Ten c.c. of the solution are then treated exactly as in the standardisation of the copper solution. If it is not possible to adjust the concentration of the sugar solution without destroying some of the reducing power, the amount of copper sulphate solution used may be lessened somewhat. When tested with 5 to 6 mgrms. of pure dextrose this method showed errors of +4 to +5 per cent.; with quantities ranging from 7 to 20 mgrms. of the sugar the errors varied from −3 to +3·3 per cent. T. H. P.

Determination of Reducing Sugars in Raw Sugars, etc., by the Pot Method. H. Main. (*Int. Sugar J.*, 1932, **34**, 213–217.)—For routine determination of reducing sugars, incremental titration with Fehling's solution in presence of methylene blue as internal indicator, as described by Lane and Eynon (ANALYST, 1923, **48**, 220, 277), gives satisfactory results, but the personal element may introduce inaccuracies. Moreover, the standard method of titration given by these authors involves factors difficult to standardise, namely, the time of heating to boiling and the rate of ebullition, and, in addition, any local heating of the concentrated alkaline solution may cause destruction of both sucrose and invert sugar. The volumetric method now described overcomes these and other objections, and yields extremely accurate results in the hands of operators with a minimum of experience.

It consists essentially in heating, in boiling water, three or more large test-tubes, containing Fehling's solution, methylene blue, and such different amounts of the sugar that, at the end of a definite time, some tubes are still blue, whilst one, at least, shows complete reduction of the cupric salt. The tubes used should be of nearly the same size and weight, those employed by the author being of Monax glass and having the length 150 mm., the internal diameter 38 mm., and the weight 50 to 55 grms. Floats inserted to prevent access of air to the solutions during the determination consist of similar tubes, making a sliding fit in the others and being conveniently drawn out to a taper about 100 mm. from the closed end to make a total length of 170 mm. The water-bath may be a 3-gallon oval iron kitchen pot, tinned inside and fitted with an overflow and with a sight-feed through which hot water is added continuously to replace loss by evaporation. The water must be kept boiling. While in the water-bath, the tubes are held in clips fitted to a frame.

Use is made of Soxhlet's modification of Fehling's solution, which contains: (1) 34·639 grms. of pure crystallised copper sulphate dissolved to 500 c.c.; (2) 173 grms. of Rochelle salt and 50 grms. of sodium hydroxide dissolved to 500 c.c. Equal volumes of (1) and (2) are mixed as required. The methylene blue indicator is a 1 per cent. aqueous solution. The standard invert sugar solution is prepared as described by Lane and Eynon (*loc. cit.*), and tested as follows:—Into three of the test-tubes are placed in order: 10 ml. of Fehling's solution (into each); 24·5, 25·0 and 25·5 ml., respectively, of the diluted sugar solution, prepared by neutralising 50 ml. of the standard invert sugar solution with caustic soda solution and diluting to 250 ml.; 2 drops of methylene blue indicator. The contents of each tube are mixed by gentle rotation, the floats being then inserted so that they rest on the liquid and entrap no air-bubbles. The tubes in the frame are placed in the boiling water and removed and inspected after exactly five minutes. If the middle tube shows complete reduction, and that with 24·5 ml. of sugar solution is still blue, 10 ml. of Fehling's solution are taken as equivalent to 24·75 × 0·002 grm. = 0·0495 grm. of invert sugar. Closer approximation may be attained by lessening the differences between the volumes of sugar solution in the different tubes. The mean between the volumes in the last blue and the first red tube is always taken as correct, except that, when the blue colour in any tube is seen to fade on removal from the bath, the actual volume in that tube is regarded as the true volume.

When sucrose is present together with invert sugar, the oxidising power of the Fehling's solution is apparently decreased, probably owing to partial inversion of the sucrose. Tables are, therefore, given for the volumes of Fehling's solution reduced by solutions of invert sugar containing various proportions of sucrose. When very small amounts of reducing sugars are to be determined, the action of the Fehling's solution is accelerated by mixing it with $5N$ sodium hydroxide solution (1 vol. to 1 vol.). In this way the small percentages of invert sugar (0·01 to 0·001) in commercial white sugars may be determined accurately. The difficulty of judging the end-point in such cases, owing to the dichroism caused by the very fine state of division of the cuprous oxide, may be overcome by adding to the mixture of sugar solution and Fehling's solution, before heating, potassium ferrocyanide in the proportion of 1 mol. per 4 mols. of copper sulphate present; the ferrocyanide

(14·647 grms. of $K_4FeCy_6.3H_2O$) may be incorporated in the 500 c.c. of Fehling's solution (2) containing the Rochelle salt and sodium hydroxide. This solution keeps unchanged for months. The procedure followed is that described above, except that for sugars containing less than 0·01 per cent. of invert sugar the time of heating in the boiling water-bath is increased to 10 minutes. This modification is particularly suitable for use at night-time. A table is given also for this method of working. T. H. P.

New Volumetric Method for the Determination of Reducing Sugars. E. Haddon. (*La Revue Agricole*, 1931, No. 59, 131; *International Sugar Journal*, 1932, 34, 43.)—The determination is made on the ordinary clarified solution without de-leading. To about 100 c.c. of the solution to be examined, four drops of a 1 per cent. methylene blue solution are added, and the coloured solution is introduced into the burette. Two c.c. or 4 c.c. of a 10 per cent. solution of potassium ferrocyanide are added to 5 c.c. or 10 c.c. of Fehling's solution, and the solution is titrated by adding the coloured solution gradually without letting the boiling slacken. The end of the reaction is a *sudden* disappearance of the blue colour; it is very sharp, and the results are concordant. This method, which is a simplification of published methods, will probably be useful to sugar-house chemists, especially when determinations are to be made at night.

Quince Seed Oil. W. H. Dickhart. (*Amer. J. Pharm.*, 1932, 104, 335–336.) —*Cydonium* (quince) seeds contain about 22 per cent. of mucilage, and, when dried, about 15 per cent. of a fixed oil, amygdalin, tannin, colouring matter, and 13 per cent. of ash. As obtained by extraction with petroleum spirit a specimen of the oil had the following characteristics:—Specific gravity at 15° C., 0·9251; n_D^{40}, 1·4696; saponification value, 187·7; iodine value (Wijs), 112·4; free fatty acids (as oleic), 6·49 per cent.; unsaponifiable matter, 9·35 per cent.; n_D^{40} of free fatty acids, 1·4639; and iodine value, 100·5; total fatty acids, 90·4 per cent. The Halphen and Villavecchia tests were negative, but the Bellier test showed a trace of arachidic acid. D. G. H.

Oil from the Nuts of *Calophyllum inophyllum* (Dilo Oil). K. W. R. Glasgow. (*J. Soc. Chem. Ind.*, 1932, 51, 172–174T.)—*Calophyllum inophyllum*, a tree indigenous to Fiji, is closely related to the trees producing such oils as laurel nut, domba, and Alexandrian laurel oils; also to tacamahaca fat, and poonseed oil, Calabar, Njamplung and pinnay oils. The dry nuts contain about 40 per cent. of kernels, yielding, on extraction, about 43·5 per cent. of an amber oil, and, on a large scale by discontinuous extraction with hot ether, about 58 per cent. of oil. The oil melts at 50° C., but, when once completely melted, takes a considerable time to set again; it is a non-drying oil. The sample examined had sp.gr. at 21° C., 0·929; $n_D^{60°}$, 1·4680; saponification value, 200·9; iodine value, 81·7; free fatty acids (oleic), 33·9 per cent.; unsaponifiable matter, 0·25 per cent.; optical rotation, −9·8°. Six hours' treatment with pure oxygen decreased the iodine value to 64, the acid value remaining unaltered. The liquid and solid acids of the free acid portion were separated and examined, and these acids showed no radical difference from the acids separated from the neutral oil. The whole oil was saponified, and the liberated acids, when examined by the Twitchell method, yielded 9·7 per cent. of resin acids, only abietic acid being identified. The remaining fatty acids yielded 31 per cent. of solid, and 69 per cent. of liquid acids, and, after separation and redistillation, the 90·30 per cent. present were found to consist of palmitic, 14·1; stearic, 11·0; erucic, 3·0; oleic, 48·0; and linolic acid, 14·3 per cent. The unsaponifiable matter contained sitosterol. D. G. H.

Determination of Veronal and of Mercury Tannate. A. Ionescu-Matiu and A. Popesco. (*J. Pharm. Chim.*, 1932, **124**, 551–554.)—*Veronal*: Two to 4 c.c. of a saturated solution of veronal are treated with 5 c.c. of a mercuric sulphate solution made by dissolving 5 grms. of mercuric oxide in 20 c.c. of concentrated sulphuric acid and 93 c.c. of water. A white precipitate is formed on shaking, and, after centrifuging, the opalescent supernatant liquid is decanted, and the precipitate is washed with 3 portions of 3 to 4 c.c. of water, and, finally, dissolved in a hot mixture of sulphuric and nitric acids (strength not given), the solution on dilution to 100 c.c. remaining clear. After addition of a few drops of permanganate solution (to destroy the nitrous compounds), the mercury is precipitated with 12 drops of a 10 per cent. solution of sodium nitroprusside. By means of a microburette a 0·1 N solution of sodium chloride is added until the cloudiness has disappeared. One c.c. of 0·1 N sodium chloride solution is equivalent to 0·01393 of veronal. The amounts of veronal found by this method agreed very closely with the amounts taken.

Mercury Tannate.—The tannate (0·02 to 0·15 grm.) is treated with 10 c.c. of a hot mixture of sulphuric and nitric acids (strength not given), the clear solution is diluted to 100 c.c., a few drops of 2 per cent. potassium permanganate solution are added, followed by 20 drops of 10 per cent. sodium nitroprusside solution to precipitate the mercury. Titration with 0·1 N sodium chloride solution then follows, and the number of c.c., multiplied by the factor 0·01785, gives the amount of mercury tannate originally present. D. G. H.

Biochemical

Body Fats of the Pig. II. Some Aspects of the Formation of Animal Depôt Fats Suggested by the Composition of their Glycerides and Fatty Acids. A. Banks and T. P. Hilditch. (*Biochem. J.*, 1932, **26**, 298–308.)—The whole of the leaf fat and a complete longitudinal section of the back fat, about 20 cm. wide, from a sow, have been subjected to a detailed survey of the component glycerides in the perinephric fat and in the layers on either side of the central seam of connective tissue in the back fat. The diet of the animal for about 15 months prior to slaughter had consisted of a mixture of wheat middlings (6 to 12 parts), barley meal (2½ to 5 parts), and fish-meal (½ to 1 part), with about 1 part of either extracted soya bean meal, dried milk, or cheese. The shoulder end of the back fat was noticeably softer than the main central portion. The data for component fatty acids of the pig fats are summarised. The most notable feature is the tendency for the united molar percentage of stearic, oleic and linolic acids to be in the neighbourhood of 70 per cent. Whatever the degree of saturation of a depôt fat, its molar content of C_{18} acids is near 70 per cent. (rising to about

73 per cent. with very unsaturated fats, and falling to about 65 per cent. in the more saturated fats). The actual degree of saturation is controlled, almost wholly, by the relative amounts of stearic and oleic acids present in any given case. The relative amounts of linolic and oleic acids in any pig fat seem to depend merely upon (1) the amount of stearic acid formation which has occurred, coupled with (2) the amount of linolic acid present in the mixed fatty acids as a whole; the latter depends to a large extent on the diet, and increases, but within comparatively narrow limits, from the perinephric to the outer layers of the back fats. The occurrence of 1 to 2 per cent. of unsaturated acids of the C_{20} and C_{22} series in all the depôt fats of a pig fed on a diet including fish-meal is noteworthy. As in the case of vegetable oils, the characteristic acids of ingested animal fat appear in pig depôt fats, but the C_{20} and C_{22} acids are not stored so freely as oleic and linolic acids. The results, on the whole, corroborate the general trade experience that a fish-meal diet leads to the production of extremely soft fat; the softness is due both to general increase in unsaturated components and, especially, to unusually large proportions of linolic acid. The C_{20} and C_{22} acids are not present in sufficient quantity to add appreciably to the soft qualities of the fats, but might well, with the onset of slight rancidity, be responsible for development of a fish-like taint in the flavour. The composition of storage fats leads the authors to favour the view that a hydrogenation of glycerides rather than of free fatty acids is an essential link in the process of their formation, but where this change may take place cannot be suggested with any confidence. The authors believe that the characteristic constancy at about 70 mols. per cent. of total C_{18} acids in pig depôt fats is most closely maintained when the diet of the animal has contained only small proportions of fat, and, accordingly, this may point to fat synthesised in the animal primarily from carbohydrate as being the main seat of the suggested hydrogenation process; but this does not preclude the possibility that directly assimilated fat may also be affected. On the other hand, the evidence of Ellis and Zeller (*J. Biol. Chem.*, 1930, **89**, 185), that linolic acid in pig depôt fat is derived exclusively from assimilated vegetable linolic acid, may indicate that assimilated fat from the diet does not undergo hydrogenation to any material extent. The tendency observed, in the less saturated depôt fats of a pig, for the component fatty acids to include somewhat more than 70 mols. per cent. of C_{18} acids, and, conversely, for the C_{18} acid molar content to fall below this figure in the more saturated depôt fats from the same animal, would be explicable if specific mixtures of glycerides were selectively withdrawn from the blood at different sites of deposition. This would presuppose the presence in the blood of a common stock of glycerides in which the chemical processes had been completed, a possibility which is perhaps less remote than the alternative of hydrogenation to varying degrees in the adipose tissues themselves.

P. H. P.

Colorimetric Determination of Phosphorus. E. J. King. (*Biochem. J.*, 1932, **26**, 292–297.)—Several methods which have been described during recent years for the colorimetric determination of phosphorus are discussed. A new procedure is now proposed in which sulphuric acid is replaced by perchloric acid, which is a much better oxidising agent for the destruction of the organic material in total phosphorus determinations. The procedure is a combination of those of Martland and Robison (*Biochem. J.*, 1926, **20**, 847) and Fiske and Subbarow (*J. Biol. Chem.*, 1925, **66**, 375; ANALYST, 1926, **51**, 205), and is believed to have advantages over the methods previously described. The colour is developed at a high acidity, as recommended by Martland and Robison, which allows of considerable variation without any loss in the proportionality of colour produced; hence no allowance is necessary for the presence of moderate amounts of trichloroacetic acid in test solutions; the acid and molybdate are kept separate. The full complement of blue colour is obtained in about 5 minutes by the use of 1:2:4-amino-naphtholsulphonic acid as the reducing agent. This is the agent suggested by Fiske and Subbarow, but it is made up in a slightly different way, since it has been found impossible to keep the sulphonic acid in solution in the proportions of bisulphite and sulphite recommended. Tables show some results obtained when perchloric acid was used in the presence of several interfering substances, and total phosphorus determinations on the barium salts of several phosphoric acid esters by the perchloric acid method; barium perchlorate is soluble in water, and so the barium need not be removed before analyses are made. The solutions required are: (1) 72 per cent. or 60 per cent. perchloric acid (the strength commonly obtainable on the market). One c.c. of 72 per cent. or 1·2 c.c. of 60 per cent. perchloric acid contains almost the same "total acidity" as 1 c.c. of 30 per cent. (by volume) sulphuric acid; (2) 5 per cent. ammonium molybdate; (3) 0·2 per cent. amino-naphtholsulphonic acid; 0·5 grm. of the 1:2:4-acid, 30 grms. sodium bisulphite and 6 grms. crystalline sodium sulphite are dissolved by shaking with enough water to make 250 c.c., and the solution is filtered until clear. The solution should be freshly prepared every 2 weeks. (4) Standard phosphate. For the stock solution 2·1935 grms. of pure potassium dihydrogen phosphate are dissolved in 500 c.c. of water; this solution contains 1·0 mgrm. phosphorus per c.c. For the dilute standard solution 5 c.c. of the stock solution are diluted to 500 c.c. with water; this solution contains 0·1 mgrm. phosphorus per 10 c.c. Both solutions must be kept saturated with chloroform. To determine the inorganic phosphate an amount of the solution to be tested is measured into a 15 c.c.-volumetric flask, and water is added to about 10 c.c. One c.c. of 72 per cent., or 1·2 c.c. of 60 per cent. perchloric acid, 1 c.c. of molybdate and 0·5 c.c. of the sulphonic acid are added, and water to 15 c.c. An appropriate standard (5 or 10 c.c. of the dilute standard solution) is similarly prepared at the same time. The contents of the flasks are gently shaken between each addition, and, finally, mixed by inversion and shaking. The colours are read after 5 minutes in a Duboscq colorimeter. With trichloroacetic acid filtrates of blood, urine, and other solutions where there is no barium present, it is preferable to use a mixed solution of 5 per cent. ammonium molybdate in 15 per cent. (by volume) sulphuric acid. Five or 10 c.c. of protein-free blood-filtrate, or 0·2 or 0·5 c.c. of urine are treated with 2 c.c. of the molybdate-sulphuric acid mixture, 0·5 c.c. of the sulphonic acid and water to 15 c.c. For total phosphate the sample is measured into an acid-resistant glass boiling-tube of about 1 × 6 in., 1·2 c.c. of 60 per cent. perchloric acid are added, and the contents of the tube are heated with a micro-burner or on an electric heater. The contents become concentrated, turn brown, then become colourless as the acid fumes; the organic matter is completely oxidised in a few minutes. If the amount of organic material is large, a few drops of nitric acid, or of 30 per cent. hydrogen peroxide may be needed, and thus a little longer heating. The cooled contents of the tube are washed with several portions of water into a 15 c.c.-volumetric flask. To compensate for the loss during heating 0·2 c.c. of perchloric acid is added. One c.c. of molybdate and 0·5 c.c. of the sulphonic acid are then added to the test solution, and at the same time a standard is prepared from an appropriate number of c.c. of the dilute standard solution, 1·2 c.c. of perchloric acid, 1 c.c. of molybdate, and 0·5 c.c. of the sulphonic acid. The solution under examination and the standard are diluted to the mark, mixed, and read after 5 minutes. P. H. P.

Interpretation of the Colour Match in the Antimony Trichloride Test for Vitamin *A*. R. S. Morgan. (*Biochem. J.*, 1932, **26**, 377–380.)—It is known that the vitamin *A* potencies of very potent oils and concentrates, compared with a medicinal oil as standard, are lower than would be expected from their blue values. It is also known that the blue value of a medicinal grade oil determined *via* the unsaponifiable fraction is higher than the blue value determined directly. These discrepancies are attributed to the influence of varying colour quality on the blue component of the colour match. It is shown that the blue reading in the Lovibond match of a copper sulphate solution varies widely as the quality of the light from the solution is varied by the interposition of red glasses. The variation obtained is similar to that given in the colour matches on a wide range of oils and concentrates. It is also shown that the value for "blue *minus* yellow" can be expected to remain constant, however the redness of the solution varies, and it is considered that the value "blue *minus* yellow" would be a better criterion of vitamin *A* than the blue value as usually read. Biological tests and the fact that the "blue *minus* yellow" value of an oil determined *via* the unsaponifiable fraction agrees with the value determined directly, support this conclusion. Coward, Dyer, Morton and Gaddum (*Biochem. J.*, 1931, **25**, 1102; ANALYST, 1931, **56**, 821) compared the vitamin *A* potencies of 11 cod-liver oils and 2 concentrates, as biologically determined, with (among other things) the blue value of the oil determined directly and indirectly *via* the unsaponifiable matter. The blue value determined *via* the unsaponifiable matter gave better agreement with the biological determination of vitamin *A* than did the blue value determined directly. The author has examined oil A and oil L in the series assayed by Coward *et al.*; the colour matches determined were:

Oil A.	Oil L.
0·2 c.c. of a 10 per cent. solution: 5·5 blue + 0·4 yellow.	0·2 c.c. of a 0·35 per cent. solution: 5·5 blue + 2·5 yellow − 0·8 neutral.
Blue value = 11·0.	Blue value = 314.
"Blue *minus* yellow" value = 10·2.	"Blue *minus* yellow" value = 171.

The ratio of the blue values of these oils is oil L/oil A = 28·5/1, and the ratio of the "blue *minus* yellow" values is 16·8/1. The ratio of their biological values is given by Coward *et al.* as 15·6/1. P. H. P.

Vitamin Studies V. Chemical Methods for the Determination of Vitamins. I. Bezssonoff's Reaction. F. V. v. Hahn and M. Wieben. (*Z. Unters. Lebensm.*, 1932, **63**, 481–495.)—The work dealing with Bezssonoff's chemical reaction for vitamin *C* (ANALYST, 1921, **46**, 411, 462; 1924, **49**, 594;

1925, 50, 517), and the quantitative modification proposed by Glassmann and Posdeew (*id.*, 1929, 54, 432) are described and discussed, and it is concluded that the method has not yet been completely evaluated. Comparative tests were, therefore, made on guinea-pigs fed on a basal diet containing only traces of vitamin *C* and consisting of hay-extract, condensed milk (1:10) autoclaved at 130° C., egg-yolk, and freshly pressed yeast autolysed at 40° C., 23 samples of various fruits, 52 of vegetables, 20 of orange juice and 18 of preserves being tested. Where the guinea-pig unit was below 10, the percentages of samples giving a negative, weak, medium and strong Bezssonoff reaction were 30, 40, 30 and 0, respectively, the corresponding figures being 20, 30, 40 and 10 for 10 to 25 units; 0, 25, 60 and 15 for 25 to 100 units; and 0, 0, 30 and 70 for over 100 units. For 1:10 dilutions of sample there were 81, 77, 55 and 27 per cent. of negative reactions, respectively, and no strong reactions. The correspondence between the sugar content and the colour produced in the reaction observed by Glassmann and Posdeew (*loc. cit.*) was not confirmed. It is concluded that the reaction gives a rough indication of relative vitamin *C* contents, but must be judged with caution, as there are striking exceptions. Thus, pineapples and tomatoes give a strong reaction, but a low figure in tests on animals, whilst for black currants and many preserves these positions are reversed. Good agreement was obtained for spinach, and particularly for orange juices. The effect of cooking on vegetables was to lower both values, except in the case of Brussels sprouts, with which the biological value was unchanged and Bezssonoff's reaction was increased. J. G.

Accumulation of Molybdenum in Aquatic Plants. H. ter Meulen. (*Rec. Trav. Chim. Pays-Bas*, 1932, 51, 549–550.)—The fresh-water plant *Azolla*, together with the small alga, *Anabaena Azollae*, with which it grows in symbiosis in the small canals about Delft, contains 1·13 mgrm. of molybdenum per kilo of dry material, the canal water itself containing only 0·0009 mgrm. of the metal per litre. The molybdenum probably plays a part in the fixation of atmospheric nitrogen by the alga. T. H. P.

Bacteriological

Viability of *Coli* Bacteria in Beer. R. Koch. (*Woch. Brau.*, 1932, 49, 110–112, 116–120; *J. Inst. Brewing*, 1932, 38, 335–336.)—Pale lager beer was inoculated with about 1,000 million *B. coli* or related bacteria (10 strains) per c.c., with the result that the number fell below 1 million per c.c. after 5 to 25 days (according to the strain) at room temperature. The rate of decrease was slower at 4 to 5° C., in accordance with the general rule that antiseptics are less potent at low temperatures, but it was greater for more acidic beers (*e.g.* dark lagers). All cultures with a *p*H value over 4·4 contained *B. coli* after 25 days in the warm or cold, but at *p*H 3·6 to 3·8 the bacteria died within 15 days at room temperature, though they were still detectable after 25 days at 5° C.; for *p*H 3·0 to 3·2 they died within 5 days at 20° C., or within 15 days at 4° C. It is concluded that the acidity is the chief antiseptic influence in beer, the alcohol and carbon dioxide being of less importance. The inoculations were always very much greater than could occur in brewing practice, even if the beer-bottles were rinsed with water containing one *B. coli* per c.c. In addition, the highly dangerous organisms which are sometimes found with *B. coli* of faecal origin occur in much smaller numbers than *B. coli*, and are destroyed even more rapidly in beer. J. G.

Detection of the Incipient Decomposition of Meat. G. Brotzu. (*Z. Unters. Lebensm.*, **1932, 63, 503–514.**)—The various proposed methods are criticised and compared for a number of samples of fresh and frozen meats stored for various periods (*cf.* Ottolenghi, *id.*, **1913, 26**, 728; Grünhut, *id.*, **1919, 37**, 304; Henriques and Gjaldbäk, *Z. physiol. Chem.*, 1911, **75**, 363; Tillmans, Strohecker and Schütze, ANALYST, 1922, **47**, 78; Tillmans, Hirsch and Kuhn, *id.*, 1927, **52**, 289, etc.). If the amino acids are determined by the method of Ottolenghi or of Sörensen on 100 grms. of sample dried at 70° C., then the presence of 300 to 350 mgrms. of amino acid-nitrogen (based on titration to the third stage of Sörensen's method, *i.e.* to a weak red colour) indicates incipient decomposition. The methods of Grünhut and of Van Slyke also give satisfactory results and similar amino acid-time curves, 500 to 600 mgrms. being taken as a suitable limit in the latter case. The limiting *p*H value, determined on the warm meat juices, is 6·3. The data show no real distinction between fresh and frozen meat, except that in the latter case the amino acids are slightly higher. J. G.

Selective Fermentation of Glucose and Fructose by Yeast. E. R. Dawson. (*Biochem. J.*, 1932, **26**, 531–535.)—The author summarises the results published in the last decade on the selective fermentation of glucose and fructose by yeast. Willstätter and Sobotka (*Z. physiol. Chem.*, 1922, **123**, 170) expressed their results in terms of a selectivity constant $K = \frac{\ln y_0 - \ln y}{\ln z_0 - \ln z}$, where y_0 and z_0 represent the initial concentrations of glucose and fructose, and y and z represent sugar concentrations after a fermentation period, t. K is, therefore, the ratio of the separate velocity constants calculated for unimolecular reactions. The idea is expressed that the explanation of the phenomena of selective fermentation is to be found in the relative rates of fermentation of solutions containing low concentrations of the separate hexoses. According to the theory of Michaelis and Menten (*Biochem. Z.*, 1913, **49**, 333) the relative rates of reaction of two substrates competing for the same enzyme can be expressed by the formula $\frac{V_1K_2}{V_2K_1} = \frac{\ln y_0 - \ln y}{\ln z_0 - \ln z}$, where K_1 and K_2 are the Michaelis constants (expressed in concentrations) of the two substrates, and V_1 and V_2 the maximum velocities for each substrate alone. Since the maximum rates of fermentation of glucose and fructose by brewer's yeast are equal, it is evident that the above equation is identical with that used by Willstätter and Sobotka to express selectivity. The selectivity constant thus represents the ratio of the affinities of the two sugars for the enzyme. The author then analyses data obtained by Hopkins (*Biochem. J.*, 1931, **25**, 245), applies the Michaelis equation, and shows that the phenomena of selective fermentation by living yeast can be satisfactorily explained by the Michaelis theory of enzyme affinity. Living yeast possesses the power of adapting itself to the medium in which it is propagated, and this type of adaptation must be considered as being due to an alteration in the affinity of the enzyme for the proffered substrate. The hypothesis is advanced that the selectivity shown by zymin when fermenting mixtures of glucose and fructose is controlled by the phosphate concentration. The author states that his treatment is no more than an outline of the methods by which it may be possible to arrive at an understanding of the factors which govern selective fermentation. P. H. P.

Toxicological

Distribution and Elimination of Bismuth in the Body. Paget, Langeron and Devriendt. (*J. Pharm. Chim.*, 1932, **124**, 600–608.)—Bismuth is found in the urine and faeces within 24 hours of injection, and elimination may last over a long period; for example, the period of elimination of 8 cgrms. of a preparation of metallic bismuth lasted in one case for 23 days after the last injection. The rate of elimination appears greatest for the camphocarbonate, and the maximum rate is usually observed 3 to 4 days after injection. Bismuth may also be excreted in the saliva, and 8 days after injection of 1 c.c. of a preparation of metallic bismuth traces were found in the saliva, blood and cephalic membrane of a syphilitic patient. Bismuth is, in fact, found in all the liquids of the organism, and the liver and kidneys appear to be the most retentive organs, the brain retaining but little. D. G. H.

Organic Analysis

Thionylaniline as an Organic Reagent and its use for Identifying Acids as Anilides. P. Carré and D. Libermann. (*Compt. rend.*, 1932, **194**, 2218–2220.)—Thionylaniline is readily produced with a good yield by the action of thionylchloride on aniline hydrochloride in benzene. Alcohols do not react with it, but many acids, on heating, form the corresponding anilides. The saturated fatty acids react readily; the aromatic acids yield only small quantities of the anilides, but give colour reactions. The presence of an unsaturated bond may interfere with the reaction, cinnamic acid, for example, giving a complicated reaction, with liberation of sulphur dioxide, hydrogen sulphide and resins. If, however, the unsaturated bond is sufficiently far removed from the acid radicle the reaction is not affected, so that oleic acid is transformed into anilide under the same conditions as the saturated fatty acids. Dibasic acids also react, oxalic, phthalic, succinic, glutaric and sebacic acids giving the corresponding anilides, but malonic acid yields only non-crystalline resinous products, and the reagent should not be used for this acid series. D. G. H.

Refractive Index of Tung Oil. J. Rinse. (*Rec. Trav. Chim. Pays-Bas*, 1932, **51**, 529–532.)—Krumbhaar's statement (*Chem.-Ztg.*, 1916, **40**, 937) that the refractive index of tung oil falls from 1·518 to 1·446 when the oil is heated for 4 hours at 200° C. is denied, a lowering to only 1·510 being observed; such lowering is not influenced by the acid value. Below 200° C. the rate of polymerisation of the oil is low. At higher temperatures the rate increases at first and decreases before gelation occurs. When the oil is heated at various temperatures, ranging from 249° to 306° C., the final value of the refractive index is highest for the lowest temperature, the decrease being 0·0085 at 249° C. and 0·0109 at 306° C.; the times of gelation are 38 and 7·2 minutes, respectively. Addition of sulphur to the oil retards or prevents solidification, and the resulting oil differs markedly from the original oil, as it does not dry as quickly as the ordinary heated oil, and remains tacky for a long period. Polymerisation, caused by heating the oil in presence of a small proportion of sulphur as catalyst, is accompanied by a considerable heat effect. The mechanism of the action of sulphur is not understood, but possibly the double bonds are activated by the sulphur, giving a polymerised product quite different from that formed by the action of heat alone. T. H. P.

Inorganic Analysis

Use of Solid Cadmium Amalgam in Volumetric Analysis. S. Kaneko and C. Nemoto. (*J. Soc. Chem. Ind., Japan*, 1932, **35**, 185B.)—The solution to be reduced is treated with dilute sulphuric acid and 20 grms. of cadmium amalgam (15 per cent. Cd), and a little sodium carbonate to displace the air in the flask. The solution is warmed and shaken, the amalgam liquefying. When reduction is complete, the flask is cooled with a platinum wire inserted in contact with the amalgam, which adheres to the wire on solidifying and can thus be withdrawn. The technique was applied to the determination of iron in ferric alum and of molybdenum in ammonium molybdate. W. R. S.

Determination of Antimony in Copper and Copper Alloys. W. Boehm and W. Raetsch. (*Z. anal. Chem.*, 1932, **88**, 321–324.)—The customary procedure for the determination of minute quantities of antimony in copper, brass, and bronze consists in the addition of a little ferric alum to the nitrate solution and precipitation with excess of ammonia, the ferric hydroxide acting as a collector for the antimony (Brownson, *Z. angew. Chem.*, 1914, **27**, II, 83). The method was criticised by Blumenthal (*Z. anal. Chem.*, 1928, **74**, 33). The authors, however, were unable to detect any antimony by Blumenthal's permanganate method in the ammoniacal filtrates from iron precipitates obtained as above in the analysis of alloys. If, on the other hand, the process was carried out with pure copper solutions with addition of small amounts of potassium antimonate, the recovery of antimony was incomplete. Blumenthal's unfavourable opinion of the iron method is explained by the fact that he carried out his test analyses, not with antimony-bearing alloys, but with copper solutions to which small quantities of potassium antimonate had been added. The authors regard the iron method as reliable.

W. R. S.

Rapid Determination of Tin in Ferrotungsten and Wolframite. K. Kiefer. (*Z. anal. Chem.*, 1932, **88**, 243–249.)—The finely-powdered material (5 grms.) is fused with sodium peroxide in a steel crucible; the melt is dissolved in 150 c.c. of water, and transferred with a minimum of water to a measuring 500-c.c. flask. Strong hydrochloric acid (200 c.c.) is poured on top of the alkaline liquid, and the two layers are gradually mixed by shaking, when the bulk of the tungstic acid thereby is precipitated in a pulverulent form. The higher chlorides of manganese are reduced with pure iron turnings, the solution is cooled, the volume adjusted, and the solution filtered. Two hundred c.c. of filtrate are transferred to a conical flask and treated, during cooling, with 1·3 grm. of fine aluminium powder. The liquid is heated to effect reduction and also complete solution of the aluminium, and treated, drop by drop, while hot, with a solution of 130 grms. of ferric chloride per litre of dilute hydrochloric acid, until the yellow colour of the ferric salt is distinctly recognisable. Tungstic acid is thus precipitated almost quantitatively. After 10 minutes' standing the solution is filtered through pulp, which is washed with hydrochloric acid (1:3). The filtrate is treated with 0·2 grm. of aluminium powder and 30 c.c. of strong hydrochloric acid, and the determination is concluded by the usual procedure for the titration of tin with iodine. The iodine solution must be standardised against tungsten ore or alloy, the tin-content of which has been accurately determined by Powell's method (*J. Soc. Chem. Ind.*, 1918, **37**, 285T), the iodine required being slightly in excess of the stoichiometric quantity. This is due to a little tungsten escaping precipitation. The time required for a determination is 2½ hours. W. R. S.

Use of the Antimony Electrode in the Electrometric Determination of Magnesium. B. B. Malvea and J. R. Withrow. (*J. Amer. Chem. Soc.*, 1932, **54**, 2243–2247.)—Measured mixtures of solutions of magnesium and calcium chlorides of known strengths were diluted to 150 c.c. and acidified to methyl orange with dilute hydrochloric acid. The E.M.F. was then read, using a calomel half-cell and an antimony electrode prepared from commercial stick antimony sand-papered to a smooth surface; 0·1 or 1·0 N sodium hydroxide solution was added 0·2 c.c. at a time, 2 to 10 minutes being allowed in each case for the E.M.F. (E) to become constant. E was plotted against the alkali added (v), and the resulting curves showed two points of inflexion corresponding with the beginning and the end of the precipitation of magnesium hydroxide. The values of v at the actual points are best determined by plotting $\Delta E/\Delta v$ against v; the difference between the volumes corresponding with the two well-defined peaks of the curve thus obtained gives the alkali required to precipitate the magnesium. The method gives results agreeing well with those obtained by the hydrogen electrode, without the difficulties of manipulation, and it may be used for solutions containing eight to twenty-five times more calcium than magnesium. The minimum concentration is 0·1 grm. of MgO in 150 c.c., but at low dilutions an equivalent quantity of calcium produces unsatisfactory results. J. G.

Volumetric Determination of Sodium. N. H. Furman, E. R. Caley and I. C. Schoonover. (*J. Amer. Chem. Soc.*, 1932, **54**, 1344–1349.)—The method comprises the following steps: Precipitation of the sodium as sodium magnesium uranyl acetate, $NaMg(UO_2)_3(C_2H_3O_2)_9$; reduction of the uranium in the precipitate by metallic zinc (Jones's reductor); aeration of the solution to convert a small fraction of trivalent into tetravalent uranium; oxidation of the tetravalent to hexavalent uranium by a measured excess of standard ceric sulphate solution; potentiometric titration of the excess of ceric salt with ferrous sulphate. The process is claimed to be advantageous for quantities of sodium not exceeding 0·01 grm. For manipulative details the original paper should be consulted. (*Cf.* ANALYST, 1931, **56**, 764; 1930, **55**, 527.) W. R. S.

Determination of Silica in Silicates. N. A. Tananaeff and F. I. Pertschik. (*Z. anal. Chem.*, 1932, **88**, 348–352.)—The determination is one by difference, the silica being converted into volatile fluoride and the residual fluorides converted into phosphates by successive treatment with oxalic acid and sodium metaphosphate. A determination can be carried out in 6 hours; an accuracy of about 0·2 per cent. is claimed. The silicate should contain less than 15 per cent. of alumina, otherwise high results are obtained. The sodium metaphosphate is made from pure microcosmic salt. This is heated in a platinum dish or crucible, finally over a blast burner, until the molten mass no longer evolves gas bubbles; the mass is poured out on to a clean metal plate, broken into small pieces, and kept in a desiccator for use. For the determination, one grm. of fine powder in a tared platinum crucible is moistened with water and attacked in the cold with 5 c.c. of hydrofluoric acid; the crucible is next placed on a water-bath, and the contents stirred with a platinum rod. More hydrofluoric acid is added if required. The liquid is evaporated to dryness and the residue intimately mixed with 2 grms. of finely-powdered oxalic acid. The covered crucible is heated in an oven at 120° C., and the temperature raised to 200° C., when the oxalic acid will be volatilised. The treatment with oxalic acid is repeated. An accurately weighed quantity of sodium metaphosphate (2 to 3 grms.) is added, and the crucible gently heated until the salt melts. Fusion is continued at higher temperature until constancy of weight is reached. The weight, less that of the crucible and the added metaphosphate, represents the oxides other than silica in the silicate. W. R. S.

Detection of the Acids of Arsenic and Phosphorus. N. A. Tananaeff and C. N. Potschinok. (*Z. anal. Chem.*, 1932, **88**, 271–278.)—A procedure is given for the detection of arsenic, arsenious, phosphoric, and phosphorous (hypophosphorous) acids in presence of each other and of other anions. The neutral or faintly alkaline solution is stirred and treated with 2 *N* ammonium chloride; any precipitate (silica) is filtered or centrifuged off, and the clear liquid is treated with magnesia mixture. The precipitate is collected, washed with dilute ammonia and dissolved in acetic acid, and the solution (2 c.c.) is divided into two portions: the first is treated with 0·5 to 1 c.c. of strong acetic acid and 0·1 *N* silver nitrate solution is added, drop by drop. A red-brown precipitate or coloration proves the presence of arsenic acid. The second portion is reduced with sodium sulphite and treated with 4 drops of nitric acid and ammonium molybdate; a yellow precipitate indicates phosphoric acid. The filtrate from the magnesium precipitate is oxidised with hydrogen peroxide; a fresh crystalline precipitate proves that arsenious or (hypo) phosphorous acid, or both, are present. The precipitate is collected and tested for arsenic and phosphorus as explained above. W. R. S.

Microchemical

Micro-analytical Methods in Industrial Laboratories. II. Pregl's Method of Combustion of Carbon and Hydrogen, without the use of Air. F. Vetter. (*Mikrochem.*, 1932, **10**, 109–113.)—Pregl's method is used unaltered for the combustion of an optimum amount of 3 to 5 mgrms. of material, with the exception that the absorption tubes are weighed full of oxygen instead of air. After the tube has been pre-heated in oxygen, the absorption tubes are attached, and oxygen is passed through the apparatus for ten minutes. The tubes are then left for ten minutes before being wiped and weighed. The combustion is made by the Pregl method, and takes ten minutes, after which, instead of air being passed through the tubes, the heating is continued for a further ten minutes (equivalent to 40 c.c. of oxygen) in a stream of oxygen. The tubes are then disconnected and weighed as before. Owing to the low rate of diffusion through the constrictions in the absorption tubes, results are obtained which are as accurate as when the original method is used. It is important that the constrictions and perforations in the absorption tubes should have the correct dimensions (constriction, 0·1 to 0·2 mm.; perforation, 0·2 to 0·3 mm.); otherwise inaccurate results are obtained. The advantages of the method are that the use of pure air is dispensed with, and this is of importance in a factory where the air is contaminated; also the time of analysis is shortened by 15 minutes. General precautions to remember in the analysis are:—(1) The weight of substance burnt should not be more than 5 mgrms., preferably 3 to 4 mgrms. (2) The movable wire gauze should never be omitted when heating with the movable burner. Silica tubes are unsuitable. (3) The rubber connection between the combustion tube and water-absorption tube should be left on the combustion tube between analyses, otherwise its hygroscopic properties cause errors. J. W. B.

Micro-analytical Methods in Industrial Laboratories. III. Micro-apparatus for the Gravimetric Determination of Water in Coal and other Solids. F. Vetter. (*Mikrochem.*, 1932, **10**, 407–408.)—The substance is heated to 110° C. in a boat in a short tube (10 cm. long) of Jena hard glass. The tube is heated by means of toluene vapour (or other suitable gas), which passes through an outer mantle which surrounds the tube. The water vapour to be weighed is carried over in a stream of an inert gas, such as nitrogen, into a Pregl absorption tube, containing calcium chloride, which is weighed full of nitrogen before and after the experiment. The nitrogen is passed through a pressure regulator, a bubble counter (so that the stream can be measured, as it should flow at 3 to 4 cm. per minute), then through calcium chloride, which should have the same vapour tension as that in the absorption tube, and, finally, through a tube with a glass stopper. This stopper is fitted outside the heating tube, to avoid contamination by lubricants. The exit end of the heating tube is drawn out to a tube of the same dimensions as the tip of the absorption tube, so that glass can touch glass inside the rubber connection. The absorption tube is connected with a Marriotte flask to regulate the flow of gases. The apparatus may also be used for drying under reduced pressure. This method is preferable to the methods in which the loss of weight of the material is taken as the water-content, especially for hygroscopic substances which take up water appreciably, even when weighed in a boat in a stoppered bottle. J. W. B.

Micro-extraction Apparatus (for Examination of Paintings, etc.). H. Hetterich. (*Mikrochem.*, 1932, 10, 379–383.)—A micro-extraction apparatus is designed which is suitable for separating the pigment and medium in the scientific examination of paintings. It consists of a small glass tube, 1 cm. in diameter, joined to a narrower tube, 1 cm. long and 0·4 cm. in diameter, sealed at the bottom. The solvent is placed in the narrow tube. The wider tube is 1·5 cm. long, and a small Gooch plate (0·6 cm. in diameter), with 15 perforations, rests on four projections of glass inside it, just above the narrow tube. The apparatus is fitted with a cork and condenser tube. The substance to be extracted is placed on a small filter paper, moistened with the solvent, placed flat on the Gooch plate, and held in position by a glass Gooch holder. The narrow tube containing the solvent is heated over the water-bath in a metal holder similar to that used by Emich for micro test tubes (*Recent Advances in Analytical Chemistry*, Vol. II, 1931, p. 324). An example is given of the extraction of the material used in an Ancient Egyptian wall painting. The sample was extracted for half-an-hour with chloroform, the solution was removed from the narrow tube with a fine capillary, and the medium used in the painting was then easily shown to be beeswax. After extraction the residue is also more easily identified. J. W. B.

Reviews

THE DONNAN EQUILIBRIA. By T. R. BOLAM, D.Sc. Pp. vii+154. London: G. Bell & Sons, Ltd. 1932. Price 9s.

As the result of the labours of many chemists, such as the late Jacques Loeb and the late Professor Procter, the so-called "Donnan equilibria" have been found to enter into many phenomena associated with the living process and with colloids generally. The interest thus aroused in this subject has been responsible for a considerable amount of research, particularly in more recent years. The present time is, therefore, fitting for the compilation of an adequate review of the existing literature, and this Dr. Bolam has very successfully done.

The volume consists of four chapters. In the first, there is developed the simple thermodynamic theory of the variations in osmotic pressure and electrical potential that occur at a membrane separating two solutions, one of which contains a non-diffusible ion. This follows the lines originally adopted by Professor Donnan, but, as the author states, they refer to ideal solutions only, and, in consequence, he has introduced the concept of "activity" in order that the Donnan Theory shall be of both general and strict application. The second chapter deals chiefly with the applications to general chemistry, though it is here that the fundamental work on gelatin and proteins is accorded brief discussion. Chapter III treats of some biological and technical applications, such as equilibria, occurring in the blood and other body fluids, the nature of enzymes, the manufacture of leather (including the Procter–Wilson theory of swelling of gels), and dyeing. The last chapter, which is a short one, is devoted to certain applications which, at the present stage of development, are chiefly of physico-chemical interest, such as the use of Svedberg's "Ultracentrifuge" and the viscosity of protein solutions.

Throughout the book the matter has been admirably arranged, condensed and presented. It is just possible that in places the treatment is too sketchy, and a little more by way of explanation would have been an advantage to the general chemist. The book may be strongly recommended to all students preparing for special degrees in chemistry. It should also find a place in the library of older chemists who desire to know something of one of the more important trends of modern chemistry.

H. T. S. BRITTON

HYDROGEN IONS. THEIR DETERMINATION AND IMPORTANCE IN PURE AND INDUSTRIAL CHEMISTRY. By HUBERT T. S. BRITTON, D.Sc., F.I.C. Second Edition. Pp. xvi+589. London: Chapman & Hall. 1932. Price 25s.

There are few chemists to-day who, in one way or another, are not concerned with *p*H determinations; consequently the second edition of Dr. Britton's book will be welcomed by all. There have been no fundamental alterations in the character of the book, but, where necessary, fresh paragraphs have been introduced in order to bring the information completely up to date. The new work that has been published since the appearance of the first edition, two-and-a-half years ago, has necessitated increasing the size of the volume by nearly eighty pages.

The first fifteen chapters are devoted to the fundamental principles of the subject and the practical details for the determination of hydrogen ion concentrations by the potentiometric and colorimetric methods. As readers of the first edition will recollect, the facts are presented in a clear and simple manner, and the description of experimental methods is sufficiently precise to enable measurements to be undertaken without reference to the literature. Where further details are required, students will find that the references given in the text are both exhaustive and up-to-date. The section dealing with the measurement of E.M.F., employing thermionic valve circuits, has been considerably enlarged. The extremely small currents that are taken by valve circuits renders them very suitable for measuring the E.M.F. of cells that are readily polarised, or have an exceptionally high internal resistance, as is the case when a glass electrode is employed. It seems certain that the possibilities of such circuits will soon be more generally realised, and that they will be employed in preference to the Lindemann electrometer, which is generally used at the present time.

A serious weakness of the first edition was the omission of any mention of modern theories of electrolytes and, arising from this, the use of concentration terms in expressions where strictly the activities of the ions should have been employed. This defect has been largely overcome by the introduction of an extra chapter by Dr. R. A. Robinson on "Recent Theories of Electrolytic Solutions, the Influence of Neutral Salts." Useful summaries are given of the conception of affinity, the Debye-Hückel theory, and the experimental measurements of neutral salt effect. The limited space available does not permit anything more than a bare outline of the modifications introduced by these theories to be given. However, in a textbook of applied science this is hardly a disadvantage, as the reader will not be confused by superfluous theory.

The latter half of the volume is devoted to a consideration of the importance of hydrogen-ion concentration in industrial and laboratory processes. Two new chapters are found here on "The Precipitation of Sulphides" and "The Hydrogen Ion Concentration of Hens' Eggs." These titles give a fair indication of the scope of this section of the book; there are seventeen chapters in which the importance of *p*H determinations in all branches of industry is dealt with. The book can be thoroughly recommended, and should find a place on the shelves of most libraries, whether private or public. R. H. PURCELL

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Fifth Edition. Edited by C. AINSWORTH MITCHELL, M.A., D.Sc., F.I.C. Vol. IX. Pp. 617. London: J. & A. Churchill. 1932. Price 32s.

All the volumes of "Allen" are full of good matter and are well-nigh indispensable to the analyst, but some contain more matter in everyday use than others. Volume IX is one of the most useful, and full of "meat" in more senses than one; those who deal with foodstuffs will find it invaluable, for no other single book, so far as the reviewer is aware, contains so much information on plant foods, plant proteins, milk, milk-products, cheese, meat, meat-products, eggs, fish and kindred topics. The contributors are Dr. Jordan Lloyd, Mr. Elsdon, Captain Golding, Mr. Bolton, and Dr. R. Moulton, all names well known in their respective spheres, and Dr. Mitchell has woven together their contributions with his accustomed skill. There is very much new matter in this volume: its bulk is increased by 113 pages, and most, but not quite all, obsolete matter has been excised, so it has not been possible, as had been intended, to complete the edition in nine volumes, and a tenth is in preparation, which will include, amongst other subjects, haemoglobin, scleroproteins, vitamins, woods, therapeutic-organic preparations, and a general index.

By far the most important sections here are those on milk, milk-products and meat-products. Mr. Elsdon, who has revised Dr. Van Slyke's former contribution, makes an excellent summary of the three principal milk proteins, dealing at length with casein, and briefly with albumin and globulin; the recent work of Moir is included. Capt. Golding deals all too briefly with milk, its variations, analysis and adulteration; he outlines the freezing-point method for detecting added water, but one could wish he had dealt more fully with this thorny problem, and given a clear opinion on all the available methods. The detection and significance of nitrates have unfortunately been omitted; also, there is no mention of the analysis of altered or sour milk; this problem, though quite old, is still with us, and the accepted methods ought to be described. The subject of graded milk comes within the purview of the analyst, and needs description and discussion of methods of testing.

Mr. Bolton deals very thoroughly with milk-products, and besides the well-known ones, such as cream, condensed milk and cheese, gives useful information on many interesting, if recondite, points; where else can the analyst find all about mazum and yoghourt? One would like to draw him out more fully on infant foods and the analysis of pasteurised cheese. Van Slyke's book on cheese is unfortunately omitted in the bibliography (on cheese), and it is the best. It is sad to observe that 23 countries have legislative standards for cheese, but England still has none.

The largest section deals with meat-products, and this is admirably done. There are up-to-date tables of composition of the different kinds of meats, including their mineral constituents; the identification of different species of meat used for food by serological methods is well, but briefly, described, as are also their microscopical characteristics. In this connection it is odd that of the eight illustrations of muscle fibres, four are human and three others muscle of a dog, frog and wasp; for the ox, sheep, etc., we are referred to "Meat through the Microscope." Details are given of the best methods for examining meat extracts and of supposed unsound meat products, also pickled and cured meats and sausages. Metallic contamination, colouring matters and preservatives and their determination are well described.

About forty pages are devoted to eggs, both fresh and dried, and give valuable data not found in most other books; the section concludes with twenty pages on fish. Altogether, this is an excellent contribution.

Quite naturally one might comment on details of omission or many small points, but sufficient has been said to indicate that the volume, as a whole, is excellent, and one of the most useful of the series. Volume X will be awaited with interest.

Alfred H. Allen died in 1904, but "Allen" is still living and going strong in 1932.

H. E. Cox

STRUCTURE AND COMPOSITION OF FOODS. By ANDREW L. WINTON, Ph.D., and KATE BARBER WINTON, Ph.D. Volume I. CEREALS, NUTS AND OIL SEEDS. Pp. 710. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1932. Price 53s. net.

No one will underrate the importance of a work on the ambitious scale of "Structure and Composition of Foods," of which Volume I ("Cereals, Nuts, and Oil Seeds") is under review. Moreover, from the point of view of microscopy, any work by Winton is acceptable and authoritative. The authors' task, to quote from the preface, has been ". . . partly to collect, select, summarise, and unify, so far as expedient, results . . . scattered through numerous journals, and partly to add their own contributions, largely hitherto unpublished, on the gross and microscopic structure. . . ." The method of treatment is particularly interesting, the scientific matter being considered under three main heads: (1) Macroscopic structure, (2) microscopic structure, (3) chemical composition. "The chief mission of the work," the authors state, is "the exploiting of the interrelation of structure or optical science to composition or chemical science." For the macroscopic and microscopic sections, all praise is due to the authors; their descriptions are clear, the choice and reproductions of sketches and photomicrographs excellent, and these alone well justify the book—although its price of 53s. appears to be very high. For the collection of chemical data, the thanks of everyone working in this field are due, but it appears to be regrettable that the authors have thought fit to discuss the chemical aspect, for it can only be concluded from statements made, that they have little intimate knowledge of the questions discussed. As an example, the following statement appears on p. 214: "The low results by the open dish method (for moisture in flour) . . . are partly but not completely nor uniformly, compensated for by the use of the conventional factor 6·25, instead of the more accurate factor 5·70" . . . the scientific connection between low moisture results and the alteration of the factor for converting nitrogen to protein being difficult to follow.

Nitrogen-free extract is a very vague term, as applied by the authors. For example, "The oat bran is the true bran of oat-groats from which the starch has been removed by washing . . . Rolled Oats, N-f-ext 65·57 per cent.; Oat bran, N-f-ext 59·90 per cent." The authors make a claim for a kind of contracted word to represent "Nitrogen-free extract." "The authors (p. 10) in their notes and conversation have adopted 'nifext'—nineteen letters, a hyphen, and a space reduced to six letters—the derivation and meaning of which should be evident even to a foreign reader. The writers, hesitating to go to the full limit in this work, have employed in table-heads the abbreviated form 'N-f-ext,' but hope that this will be a stepping-stone to the coined word 'nifext'." It is to be hoped that such will not happen, or we may look forward to "sonofts" in dairy chemistry, and to "Fafres," as representing "Fat-free-residue."

One is forced, however, to the conclusion that the book is not meant for chemists, for definitions are given which are distinctly loosely worded, *e.g.* (p. 358): "The saponification number is a measure of molecular weight or the number of carbon atoms in the acid molecule. . . ."

On p. 17, too, the statement is made, referring to the ash of plants: "When neither the content of carbon dioxide nor alkalinity of ash is given, the reader *must make a laborious calculation* in order to determine whether the ash is neutral or alkaline." (The italics are the reviewer's.)

The elements of microscopy are so widely learned by English students that the following appears to be somewhat redundant: "To chemists and others who are unfamiliar with micro-technique, and who are afflicted with a kind of 'stage fright,' it may be said that the microscope is little more complicated or difficult to operate than the opera-glass."

Notwithstanding the fact that to the chemist reading the book such points, mis-statements and loosely worded definitions as those quoted are irritating, the book is a valuable compendium of fact—apart from the opinions of the authors, and accordingly is worthy of a place on our bookshelves. L. H. LAMPITT

MONOGRAPHS ON BIOCHEMISTRY. ALCOHOLIC FERMENTATION. By Prof. ARTHUR HARDEN, F.R.S., etc. Fourth Edition. Pp. vii+243, with illustrations. London and New York: Longmans, Green & Co. 1932. Price 15s. net.

The production of ethyl alcohol by a process, termed at a very early date "fermentation" is one of the oldest chemical problems to be studied, and, in modern science, it has proved to be one of the most suggestive of all those connected with biochemistry.

The history of alcoholic fermentation may be divided into three epochs, when chemical, biological, and biochemical theories were put forward. The first was that propounded by Willis in 1659 and by Stahl in 1697. It was developed by Liebig a hundred years later. The second was placed on an irrefutable footing by Pasteur, whilst the third had its birth in the discovery of E. Buchner, that alcoholic fermentation is due to an enzyme which can be separated from yeast. Those who are familiar with the literature of the subject from the time of Buchner's great discovery will place Professor Arthur Harden in the front rank of investigators in this domain, for he, with his school, has done more to develop our knowledge of alcoholic fermentation than any other chemist of recent times.

In the nine years since the last edition of this monograph was published, a large number of papers on the subject have appeared. To the present edition 49 additional pages have been added, but the number of chapters remains the same, and the headings have not been altered.

The first two chapters, the text of which is historical, have received no revision, but the remaining eight chapters have been considerably extended and brought up-to-date.

The different enzymes of yeast, besides zymase and sucrase, are described, such as carboxylase, carboligase, and the reducing enzymes. It is stated that up to the present the following enzymes and complex substances concerned with oxidation and reduction have been detected in the yeast cell: glutathione, a dehydrogenase, a thermostable peroxidase, an indophenol oxidase, and a cytochrome system containing, as shown by Keilin, three components.

The function of phosphates in alcoholic fermentation is dealt with at length, as are also the chemical changes involved in fermentation and the mechanism of fermentation. The views of different authors on these subjects are extremely conflicting.

The accelerating action of phosphates and arsenates on the fermentation of sugars by zymase preparations was first observed by Harden and his colleagues, and this led to the discovery of the sugar phosphates. When glucose, mannose, fructose, or sucrose is fermented with yeast preparations in presence of phosphates, three well-defined compounds may be isolated: a hexose diphosphate (Harden and Young), a hexosemonophosphate (Harden and Robison), and a trehalosemonophosphate (Robison and Morgan). Neuberg has obtained a second hexosemonophosphate by the partial hydrolysis of the diphosphate. It is a much less stable substance than the monophosphate formed direct, and Meyerhof suggests that such an active phosphate is the first product to be formed in alcoholic fermentation. It seems to be well established from the work of Robison and Morgan that the diphosphate is a derivative of γ-fructose. It has not been found possible to isolate corresponding arsenates.

The chemical changes involved in fermentation are discussed at length, but the views held by different workers are here also conflicting. Whilst the book deals mainly with acellular fermentation, that brought about by the living cell is also discussed.

Those who expect to be able to use this monograph as a teaching book for elementary students may be disappointed, for the subject is all to complicated to be treated fully within the limits of space available. It is, however, a complete guide to the literature, and as such will be found invaluable by research workers and teachers.

Arthur R. Ling

Dizionario di Merceologia e di Chimica Applicata. Vol. IV. Senapa to Zucchero. By Professor G. Vittorio Villavecchia and Others. Fifth Edition, revised and enlarged. Milan: Ulrico Hoepli. 1932. Price 80 lire.

This volume, which completes the work (see The Analyst, 1930, **55**, 357; 1932, 69), contains 460 pages of text, and includes, among its contents, articles dealing with various subjects in which Italy is particularly interested, such as silk (48 pages), silk fabrics, grapes, wine (37 pages), sulphur (11 pages), etc. As in the preceding three volumes, the materials considered cover a wide range, scarcely anything of interest to industrial chemists or to dealers in, or manufacturers of, chemical products, being omitted. In addition to those which may be defined more strictly as chemical in nature, the products treated of in the present volume comprise mustard, sepia, sesamé oil, tallow, medicinal syrups and medicinal substances in general, emery, soya bean oil, solvents and plasticisers for lacquers, sumac, spices, sponges, rags, ostrich feathers, cork, suppositories, tobacco, tannins, truffles, tea; fuller's and other earths, waterproof fabrics, tinctures, hair dyes, turpentine, eggs, glass, saffron, civet, pumpkins, and a host of others. For each of these, the occurrence, preparation, and uses are described, and trade statistics are given.

The volume is completed by an index to the whole work, this containing not merely the names of the principal headings in each of five languages—Italian, French, German, English and Spanish—but, in addition, the Italian names of the very large number of substances referred to in the text of the articles. The fact that it extends to 280 pages, each of three columns, and comprises upwards of 50,000 entries, will give an indication of the exhaustive character of the index and of its great value to users of the book.

Probably no other single publication in any language furnishes such a mass of similar information, and any analyst with a general practice and with an elementary knowledge of the Italian language, would frequently find reference to its pages of advantage.

The cost of the four volumes amounts to only 260 lire or, at the existing rate of exchange, about £3 13s., which is only a fraction of the price of German or American, or even English, scientific books of corresponding magnitude. A small increase in this very moderate figure would have allowed these heavy volumes to be bound in good stiff covers, the thin card ones supplied being quite inadequate for books likely to be in daily use.

The appended list of corrigenda for the four volumes requires further slight correction in a few particulars.

T. H. Pope

SEPTEMBER, 1932 Vol. LVII., No. 678

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Obituary

JOHN CLOUGH THRESH

THE passing of John Clough Thresh marks an epoch in English public health, for he was one of the early pioneers who established the importance of hygiene in connection with the home.

Thresh was born in Wakefield in 1850, and was educated privately and at Owens College, Manchester. His early interests were centred in pharmacy and chemistry, and resulted in his attaining the degree of D.Sc., London, in 1884. Later, at the relatively mature age of 39, he graduated in medicine at the Victoria University, Manchester, and in 1896 he was awarded the gold medal for his M.D. thesis. In 1892 he obtained the Diploma of Public Health of the University of Cambridge. He was a Fellow of the Institute of Chemistry, and had been a member of the Society of Public Analysts since 1894.

Although he published numerous communications and works on various problems of preventive medicine, and was the joint author of a useful manual on preservatives in food, his scientific publications were mainly concerned with water, and his "Examination of Water and Water Supplies" is regarded as a standard work in Great Britain, and, indeed, in all countries.

He also did much research on the purification of water and the effect of water upon health, the action of water upon lead and copper (see ANALYST, 1922, **47**, 459, 500; 1924, **49**, 124; 1925, **50**, 248), and various sterilisation processes, and, as a result of his experiments, the Excess Lime Process of Water Treatment was recently sanctioned by Parliament as an efficient method for the purification of river sources.

Dr. Thresh held many important appointments. He was the first Medical Officer of Health for the County of Essex, and occupied that position for 22 years, when he was appointed Consulting Medical Officer, a post he held until, 9 years ago, ill-health compelled him to resign. He was Lecturer in Public Health at the London Hospital Medical College and Examiner in State Medicine for the University of London, and, in addition to his official appointments, he carried out an extensive consulting practice.

Dr. Thresh married in 1872, and his wife (who predeceased him) was a constant helpmeet throughout the course of a long life marked by intensive study, research and hard work. His home life was quiet and unostentatious, and those who were privileged to know him best fully realised his kindly nature and the many generous deeds which were done by him in the most unobtrusive manner.

His qualities of clear thought and capacity for hard work, coupled with his profound knowledge and experience, made Dr. Thresh in great demand as an expert witness in connection, principally, with questions relating to water supply, and his words always carried great weight with any Parliamentary Committee or Court before which he was required to appear.

All who have noted the remarkable changes in public health and in the prevention of disease which have occurred during the last fifty years will greatly deplore the death of one of the greatest pioneers in sanitary science and preventive medicine, and those who had the privilege of personal knowledge of Dr. Thresh will mourn the loss of a great teacher and the kindest of friends.

JOHN F. BEALE

Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates

XXIII. The Quantitative Separation of Tantalum, Niobium, Titanium, and Zirconium, and a New Analytical Grouping

BY W. R. SCHOELLER, PH.D., AND A. R. POWELL

(*Work done under the Analytical Investigation Scheme*)

(*Read at the Meeting, May* 4, 1932)

THIS Section concludes the work begun in Section XV (ANALYST, 1929, **54**, 453), which dealt with the qualitative separation of these four elements. We may say at once that the pyrosulphate tannin method, which was shown in the earlier paper to be a very simple and effective procedure for the qualitative separation of the elements under discussion, is not here advanced for their quantitative separation. Whilst it proved invaluable for the quantitative recovery of small amounts of earth acid contained in titania precipitates, and in that rôle was incorporated in the perfected oxalate salicylate method (Section XXI, ANALYST, 1932, **57**, 74), it did not appear to lend itself in its original form to quantitative separations involving large quantities of earth acid. Fortunately, we were spared what would probably have proved a protracted investigation, by the discovery that our new tannin method for the separation of titanium from zirconium (Section XVIII, ANALYST, 1930, 55, 605) was capable of separating not only titanium, but also tantalum, and niobium from zirconium. This is not surprising, in view of the earlier application of tannin to the separation of the earth acids from zirconia (Section XIII, ANALYST, 1928, 53, 517). Hence, the quantitative resolution of the ternary mixture (M_2O_5:TiO_2:ZrO_2) is accomplished by first eliminating ZrO_2, as shown in this paper; the binary mixture (M_2O_5:TiO_2) is then resolved into its constituents by the oxalate salicylate method (XXI, *loc. cit.*); finally, M_2O_5 is decomposed into Ta_2O_5 and Nb_2O_5 by the tannin method described in Section IV (ANALYST, 1925, 50, 485).

TANNIN AS A GROUP REAGENT.—Important developments in the application of the procedure here discussed were forecast in Section XVIII. We found that the tannin process which separates titania from zirconia, will separate titania from thoria and alumina also, and we expressed the opinion that a separation of the earth acids from thoria and alumina by the same process would be feasible. This is now fully confirmed by experiment (*vide infra*); we are, therefore, in a position to make the following important generalisation:

Tannin quantitatively precipitates tantalum, niobium, and titanium from a barely acid oxalate solution half-saturated with ammonium chloride. Zirconia, hafnia, thoria, and alumina are not precipitated under those conditions. A quantitative separation of any (or all) of the precipitable, from any (or all) of the non-precipitable, elements can thus be achieved.

The practical importance of the new group-precipitation will be appreciated when it is realised that our procedure effectively eliminates from the solution the three elements chiefly responsible for the difficulties and complications peculiar to the analysis of earth-acid minerals. We propose using the following convenient terms:

Acid tannin group (or Group *A*): Ta_2O_5, Nb_2O_5, TiO_2.

Basic tannin group (or Group *B*): ZrO_2, HfO_2, ThO_2, Al_2O_3.

The oxides of group *A* are of more *acid* nature, and are precipitated by tannin from faintly *acid* solution. The oxides of group *B* are more *basic*, and are quantitatively precipitated by tannin from the oxalate solution when it is made faintly ammoniacal. Membership of group *B* is not confined to the four elements cited, as other metals of the "third" qualitative (ammonia) group—*e.g.* ferric iron, chromium, gallium—will be found to accompany alumina in the tannin separation from group *A*. Iron has not been included in this study because it can be precipitated as sulphide from tartrate solution, and thus be separated from all the earths. Uranium, another mineral associate of the earth acids, belongs to group *B*, as will be shown in a separate communication shortly to be published.

The analytical grouping of the rare earths as major constituents of a number of earth-acid minerals remains to be considered: they cannot be included in the present classification because their oxalates are insoluble in ammonium oxalate solution. In this connection, the work of Pied (ANALYST, 1925, 50, 36) is being re-investigated, and the conclusions will be published together with other necessary data on the determination of the rare earths in earth-acid minerals.

THE SEPARATION.—The method as described in Section XVIII was found to be applicable, with uniformly good results, to a variety of oxide mixtures (see Table). It aims at complete precipitation of the titania—or, in the present case, of group *A*—in one operation. The precipitate is dissolved and re-precipitated; the filtrates from both precipitates must be tested for complete precipitation. This is readily ascertained, thanks to the characteristic colour of the tannin complexes of group *A* (yellow tantalum, red niobium and titanium precipitates). The tannin complexes of group *B*, on the other hand, are dirty-white precipitates, easily soluble in dilute acid, and they become darker upon further addition of tannin and complete neutralisation.

Fractional Precipitation.—In Section XVIII the amount of tannin required for complete titanium precipitation is given as twelve times the weight of the titania. Now, if the addition of the reagent is purposely restricted (*i.e.* to 8 to 10 times the weight of group *A* oxides), the precipitation is incomplete, but the primary tannin precipitate TP^1, containing the bulk of group *A*, is free from group *B*. It is ignited and reserved as a final separation product.

The filtrate and washings from TP^1, boiled down to the original volume, are boiled, treated with 0·25 to 0·5 grm. of tannin, and titrated with *N* ammonia until the secondary precipitate, TP^{1a}, shows a dirty grey discoloration, which indicates incipient precipitation of group *B*. The ignited precipitate, TP^1, is re-treated as in Section XVIII; the resulting precipitate TP^2 represents the balance of group *A*. $(TP^1 + TP^2)$ is leached, ignited, and weighed as $(M_2O_5 + TiO_2)$.

The combined filtrates from TP^{1a} and TP^2 contain the oxides of group *B*, which are recovered, if desired, by boiling with more tannin and a moderate excess of ammonia (*cf.* Section XVIII, *loc. cit.*, and Section XIX, ANALYST, 1931, **56**, 308).

The above simple fractionation method yields one small intermediate fraction, the re-treatment of which in a smaller bulk of solution is more convenient and precise than that of the whole of group *A*. If group *A* is quite subordinate in the original oxide mixture, it is advisable first to produce the mixed precipitate TP^{1a}, and re-treat it, as is done in Method A, Section XIII (*loc. cit.*). The only difference between that method and the present one is, that the tannin precipitation is now carried out in a solution half-saturated with ammonium chloride.

RESULTS OF TEST ANALYSES.—The two tests Nos. 8 and 12 were published in Section XVIII, and are reproduced here. In Exps. 1 to 4 the composition of the oxide mixture was unknown to the operator. This practice had to be abandoned in the later tests because we were not then working together. The column headed "Tannin" gives the amount of precipitant used for the production of TP^1. The next two columns, headed TP^1 and TP^{1a}, respectively, give the *gross* weights of the two fractions. Where no weight is entered under TP^{1a}, the whole of group *A* came down in TP^1, slightly contaminated with group *B*, and the precipitate was accordingly re-treated as in Section XVIII. The result of the re-treatment of TP^1, or TP^{1a} (where such was obtained) followed by lixiviation of the final precipitate TP^2 or combined precipitate ($TP^1 + TP^2$), is given in a single column headed "Final *P*."

Exp.	Group *A*	Taken Grm.	Group *B*	Added Grm.	Tannin Grms.	TP^1 Grm.	TP^{1a} Grm.	Final *P* Grm.	Group *A* Error Grm.
1	Ta_2O_5	0·1048	ZrO_2	0·1014	1·2	0·1072	—	0·1053	+0·0005
2	Nb_2O_5	0·1064	ZrO_2	0·1055	1·2	0·1054	0·0052	0·1062	−0·0002
3	Ta_2O_5	0·0672	ZrO_2	0·0890					
	TiO_2	0·0700			1·5				
	Σ	0·1372				0·1413	—	0·1368	−0·0004
4	Nb_2O_5	0·0515	ZrO_2	0·1486					
	TiO_2	0·0628			2·0				
	Σ	0·1143				0·1215	0·0060	0·1146	+0·0003
5	M_2O_5	0·0637	ZrO_2	0·1004					
	TiO_2	0·0551			1·5				
	Σ	0·1188				0·1259	—	0·1192	+0·0004
6	Ta_2O_5	0·1051	ThO_2	0·1042	1·0	0·1038	0·0017	0·1042	−0·0009
7	Nb_2O_5	0·1066	ThO_2	0·1028	1·0	0·0999	0·0077	0·1066	0·0000
8	TiO_2	0·0479	ThO_2	0·1068	0·8	(*a*)	—	0·0484	+0·0005
9	Ta_2O_5	0·0505	ThO_2	0·0818					
	TiO_2	0·0528			1·2				
	Σ	0·1033				0·1057	—	0·1023	−0·0010
10	Nb_2O_5	0·0628	ThO_2	0·0721					
	TiO_2	0·0433			1·2				
	Σ	0·1061				0·1055	0·0023	0·1059	−0·0002
11	Ta_2O_5	0·0551	Al_2O_3	0·2676					
	Nb_2O_5	0·0738			1·5				
	Σ	0·1289				0·1248	0·0068	0·1286	−0·0003
12	TiO_2	0·0532	Al_2O_3	0·2357	0·8	(*a*)	—	0·0528	−0·0004
13	Ta_2O_5	0·0613	Al_2O_3	0·1072					
	Nb_2O_5	0·0439			2·0				
	TiO_2	0·0534							
	Σ	0·1586				0·1584	0·0056	0·1587	+0·0001
14	Ta_2O_5	0·0431	ZrO_2	0·0567					
	Nb_2O_5	0·0303	ThO_2	0·0303	1·5				
	TiO_2	0·0380	Al_2O_3	0·0540					
	Σ	0·1114				0·1152	—	0·1112	−0·0002

(*a*) Not weighed

We submit that the tabulated results demonstrate the accuracy of the process, errors not exceeding 0·0005 grm. being recorded in 12 out of 14 tests. Further, the mode of working remained quite unaffected by the nature of the oxide mixture, which varied in composition in each experiment. The last test, involving six earths, was no more difficult than any of the tests with binary mixtures. We are not conscious of any exaggeration when we express the opinion that the process is one of the most remarkable yet discovered in the domain of the analytical chemistry of earth-forming elements. It owes its superiority to a combination of two factors: first, a clean-cut separation, based upon the more pronounced differentiation in chemical behaviour between the two groups, brought about by the conversion of the earths into their oxalo-complexes; and secondly, the certain identification of tantalum, niobium, and titanium, by means of the characteristic colour of their tannin complexes.

SUMMARY.—Our recently-published method for the separation of titanium from zirconium, based on precipitation of the titania as tannin complex from the nearly neutralised oxalate solution half-saturated with ammonium chloride, has now been proved to afford a quantitative separation of tantalum, niobium, and titanium ("acid tannin group") from zirconium, thorium, and aluminium ("basic tannin group"). Under the conditions realised by the procedure, tannin acts as a group reagent, precipitating any or all of the members of the acid tannin group, and thus separating them from any or all of the members of the basic tannin group. The inclusion of certain other metals (*e.g.* uranium) in the last-named group is being investigated.

THE SIR JOHN CASS TECHNICAL INSTITUTE,
ALDGATE, LONDON, E.C.3

A Rapid Method of Dissolving Lead Alloys Preparatory to the Determination of Tin and Antimony*

BY B. S. EVANS, M.C., PH.D., F.I.C.

WHEN a lead-tin alloy is once in solution in hydrochloric acid the determination of the tin is a relatively simple matter; in the absence of interfering metals it can be directly reduced, *e.g.* with metallic lead (A. R. Powell, *J. Soc. Chem. Ind.*, 1918, **37**, 287T), or with hypophosphorous acid (B. S. Evans, ANALYST, 1931, **56**, 171) and titrated.

To obtain the solution is, however, often a matter of considerable difficulty and delay. Finely divided lead alloys can be dissolved in a solution of bromine in hydrochloric acid; they must, however, be finely divided, as a very small lump of the alloy may delay solution for many hours; solution at best is slow, and all this time there is danger of loss of tin through volatilisation; in addition to this one can deal with only small samples.

In a former paper (ANALYST, 1927, **52**, 568) I published a method for solution of lead alloys, in lump form, in bromine with hydrochloric acid. This method would seem to constitute an advance, inasmuch as it enables one to deal with larger samples in lump form and, moreover, shortens the time required for solution; a serious drawback to it, however, is the somewhat complicated apparatus required. If we do not use hydrochloric acid as a solvent medium but try various mixtures containing nitric acid we are faced with a separation from the acid radicle; this, in itself, is no great difficulty (*cf.* B. S. Evans, ANALYST, 1932, **365**), but, in addition, there is the trouble of finding an acid mixture which will dissolve both lead and tin. Quite a small quantity of hydrochloric or sulphuric acid in the solution mixture will practically stop solution altogether, owing to the deposition of the corresponding lead salt on the metal; on the other hand, if nitric acid is used, something must be added to prevent the formation of "metastannic acid," which, once formed, would be exceedingly difficult to get into solution again (methods, of course, exist in which the "metastannic" acid is filtered off and dissolved in strong hydrochloric acid, but there is considerable danger of losing tin in the process, and even so the solution occupies some time). I have used with great success a mixture of nitric with citric or tartaric acid for dissolving lead-antimony alloys (ANALYST, 1929, 54, 404) and lead-tin alloys where the tin is present in small amount; where the amount of tin is higher, however, the amount of citric acid required to keep it in solution is prohibitive. Perchloric acid has come into prominence lately, chiefly in the United States, as a solvent for metals and an oxidising agent (*cf.* H. H. Willard and R. C. Gibson, *Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 88), and, as lead perchlorate is extremely soluble, it seemed worth while to try it as a solvent for the alloys under discussion. Lead itself dissolves rapidly and completely when the perchloric acid has become concentrated by evaporation; tin, however, and antimony form white insoluble compounds which are, apparently, of the nature of "metastannic" and "metantimonic" acids. On trying various mixtures of perchloric with other acids I found, for lead-tin alloys, that mixing perchloric acid with phosphoric acid gave a liquid with the desired properties. One final difficulty remained to be surmounted in that the tin seems to be converted into stannic chloride, and a considerable quantity of it was lost when solution was carried out in a beaker; this was overcome by carrying out the process in a flask fitted with ground-in tube acting as an air-condenser.

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* Communication from the Research Department, Woolwich

PROCESS FOR LEAD-TIN ALLOYS.—Details of the process are as follows:—A convenient amount of the sample (which may be in lump form) is placed in the flask; 15 c.c. of perchloric acid (60 per cent.) and 10 c.c. of syrupy phosphoric acid (these quantities are suitable for a sample weight of about 2 grms.) are heated in a beaker until dense white fumes appear; the beaker is then allowed to cool somewhat, and the acid mixture is poured on to the sample in the flask. The stopper carrying the condenser-tube is immediately inserted, and the top of the tube is closed with a rubber stopper carrying a glass tube connected by rubber tubing with a Mitscherlich absorption-tube containing 10 c.c. of dilute (1:1) hydrochloric acid. The liquid in the flask is now boiled gently until all the sample is dissolved; this usually takes from 10 to 15 minutes for a 2-grm. sample; if much tin is present, drops of stannic chloride can be seen condensing and running back into the solution, where apparently they react with the lead perchlorate, giving lead chloride; this lead chloride, not being on the surface of the metal, does not hinder solution in the slightest. When all the metal has been dissolved the apparatus is allowed to cool for some minutes, the bulb-tube is then detached, and the contents are poured into the reduction-flask of the tin titration apparatus described in former papers (Evans, ANALYST, 1927, 52, 570; 1931, 56, 172), and rinsed in with 10 c.c. of water; 30 c.c. of water are poured down the condenser-tube into the solution-flask, the apparatus being sloped and rotated meanwhile in order to rinse the walls; the condenser is detached, and the stopper is rinsed into the reduction-flask with a little of a mixture of 70 c.c. of dilute (1:1) hydrochloric acid and 10 c.c. of dilute (1:3) sulphuric acid; the contents of the solution-flask are then poured into the reduction flask and rinsed in with the remainder of the acid mixture. Two or three grms. of sodium hypophosphite are next added to the solution, followed by 1 c.c. of saturated mercuric chloride solution, and the flask is shaken and warmed slightly; if the smell of chlorine persists, more hypophosphite is added in small amounts, followed by shaking and warming until the smell of chlorine is entirely dispelled; finally, 4 to 5 grms. of hypophosphite are added, and the stopper (with the titration attachments) is placed in the flask; carbon dioxide is passed through the flask for 10 minutes, the solution is boiled for 15 minutes (with carbon dioxide passing), and the liquid is cooled and titrated as previously described (Evans, ANALYST, 1931, **56**, 173). Some trials were made with weighed quantities of tin and lead, with the following results:

Tin taken Grm.	Lead taken Grm.	Titration c.c.	Tin found Grm.	added Per Cent.	found Per Cent.
0·100	1·90	16·95 of $N/10$	0·1007	5·00	5·03
0·080	1·92	13·50 ,,	0·0800	4·00	4·00
0·060	1·94	10·00 ,,	0·0594	3·00	2·97
0·040	1·96	6·80 ,,	0·0404	2·00	2·02
0·020	1·98	34·2 of $N/100$	0·0203	1·00	1·01
0·010	1·99	16·6 ,,	0·0098	0·50	0·49

The total time taken for a determination was about 80 minutes.

ANALYSIS OF LEAD-BASE WHITE METAL.—The above method of solution lends itself readily to the determination of tin in white metals containing a high proportion of lead. Trials were made on "White Metal A" of Messrs. Ridsdale's "British Chemical Standards." The composition of the alloy as given on the certificate is as follows:—Lead, 82·6; antimony, 12·04; tin, 4·64; copper, 0·33; iron, 0·06; bismuth, 0·03; arsenic, 0·06; zinc, 0·08 = 99·84 per cent.

In view of the presence of copper and of a very high proportion of antimony, a partial separation of the tin was required; the following method was adopted:—A sample-weight of 2 grms. was dissolved in the manner given above; the contents of the Mitscherlich tube and one 10 c.c. washing were poured down the condenser-tube, and the latter was rinsed down with 60 c.c. of dilute (1:1) hydrochloric acid and 20 c.c. of water. Without disconnection of the condenser tube the liquid in the flask was boiled for 10 minutes, then cooled and filtered, the precipitated lead chloride being washed with 100 c.c. of 15 per cent. hydrochloric acid. To the filtrate were added 30 c.c. of citric acid solution (100 grms. dissolved in 200 c.c. of water), followed by solid sodium hydroxide in small lumps until the maximum turbidity seemed to have been produced; then sodium hydroxide solution (20 per cent.) until alkaline to litmus and 50 c.c. in excess; finally, 10 c.c. of saturated potassium cyanide solution and about 5 grms. of sodium sulphide dissolved in water. The beaker was allowed to stand on the steam-bath for about 15 minutes, after which its contents were filtered and the precipitated lead sulphide was washed with hot 5 per cent. ammonium chloride solution; 20 grms. of ammonium chloride and about 8 grms. of sodium hydrosulphite were added to the filtrate, which was then boiled for 1 minute, allowed to stand on the steam-bath for 10 minutes (with a further addition of 1 to 2 grms. of hydrosulphite), filtered hot, and the stannous sulphide precipitate dealt with as described in a former paper (Evans, ANALYST, 1932, 362). The results obtained from five determinations were as follows:

Found, 4·75, 4·69, 4·75, 4·75, 4·73; mean, 4·73 per cent.

Results of referee analysts given on certificate, 4·62, 4·94, 4·57, 4·74, 4·48, 4·67, 4·49, 4·86, 4·16, 4·83; mean, 4·64 per cent.

LEAD-ANTIMONY ALLOYS.—When the above method of solution was tried for lead-antimony alloys it quickly became manifest that something was wrong; the metal went into solution readily enough, giving a bright solution, but on attempting to determine the antimony in the solution by the bromate titration I invariably got low results. I next found that on re-reducing the same solution with sulphur dioxide and carrying through the titration afresh, I got rather higher, though still low, figures; a third titration gave results higher still, thus:

Lead taken Grm.	Antimony added Grm.	Antimony found	Grm.
1·90	0·1000	1st titration less than	0·0857
		2nd titration	0·0964
		3rd titration	0·0976

As it seemed evident that boiling with hydrochloric acid promoted better results, I treated a similar mixture in the same way, but boiled the liquid, after addition of hydrochloric acid, for half-an-hour before reducing; in this case I recovered 0·0994 grm. of the 0·1000 grm. originally added. The above figures, coupled with the fact that the product of heating such an alloy with a mixture of perchloric and phosphoric acids completely dissolves when boiled with water, seems to make it reasonably certain that antimony forms a complex with phosphoric acid, which is slowly and incompletely broken down by boiling with hydrochloric acid. This boiling with hydrochloric acid, besides giving results which were still somewhat low, seriously detracted from the value of the process by reason of the time taken up. In view of the fact that "metantimonic acid" is fairly soluble in hydrochloric acid which is not too dilute, I next tried eliminating phosphoric acid altogether and obtaining complete solution by boiling the product of the attack by perchloric acid with hydrochloric acid of approximately 1:1 strength; this modification at once proved satisfactory.

PROCESS.—The following process was worked out for 2-grm. samples; there is no reason to anticipate any trouble in using it for larger samples, but quantities, etc., and possibly the size of apparatus used might have to be modified. A suitable amount (*e.g.* 20 c.c. for 2 grms.) of perchloric acid is placed in a beaker and evaporated until the fumes given off become thick and heavy, somewhat resembling those obtained from sulphuric acid; the beaker is then allowed to cool somewhat. The weighed sample (which may be in lump form) is placed in the flask of the apparatus, described for tin-lead alloys, the evaporated perchloric acid is poured on to it, and the condenser-tube is attached. The U-tube, described in the case of tin-lead alloys, was found to be not only useless, but a source of positive danger where antimony is concerned, owing to the extraction of antimony from the rubber stopper used to attach it to the condenser-tube; it has, therefore, been discarded. The flask is now heated until the sample has been completely attacked, the lead being in solution and the antimony in the form of a white precipitate; it is next allowed to cool sufficiently to admit of the safe addition of water, and 20 c.c. of water are run down the condenser-tube, followed by 100 c.c. of dilute (1:1) hydrochloric acid. The liquid in the flask is boiled under the condenser until all of the solid is in solution, after which it is transferred to a 750-c.c. flask and rinsed in with 200 c.c. of water. A rapid stream of sulphur dioxide is passed in for a minute or two, a fragment of broken pot is added, and the solution is boiled vigorously for 25 minutes, and is then titrated with bromate solution in the ordinary way. The whole process, from the time the sample is set to dissolve, can be carried out in less than an hour. It is advisable to put through a "blank" test on pure lead, as in the series given below a small blank was found; this blank was certainly not due to the methyl orange used, as at the end-point the colourless liquid can be strongly coloured by the addition of a further three drops of methyl orange solution, and this again completely discharged by one more drop of bromate. It seems probable that the blank is due either to the incomplete elimination of the last traces of the sulphur dioxide used or, much more likely, to traces of some relatively non-volatile sulphur compound carried over in the rush of sulphur dioxide gas. The following results were obtained by this method:

Lead taken Grms.	Antimony added Grm.	Titration 1 c.c. = 0·00308 Sb c.c.	Antimony found	
			Total Grm.	Corrected for blank Grm.
1·90	0·1000	32·60	0·1004	0·0998
1·92	0·0800	26·20	0·0807	0·0801
1·94	0·0600	19·60	0·0604	0·0598
1·96	0·0400	13·15	0·0405	0·0399
1·98	0·0200	6·60	0·0203	0·0197
1·99	0·0100	3·40	0·0105	0·0099
2·00	Blank	0·20		

I also determined antimony in the British Chemical Standards White Metal A, referred to above; the method used was exactly that given for lead-antimony alloys; the following results were obtained:

Weight of alloy taken Grm.	Titration 1 c.c.=0·00308 gr. Sb. c.c.	Antimony found. Per Cent.
1·00	39·70−0·20=39·50	12·17
1·00	39·75−0·20=39·55	12·18
1·00	39·85−0·20=39·65	12·21
1·00	39·60−0·20=39·40	12·14

The results of the referee analysts given in the certificate were as follows: 12·02, 12·02, 12·00, 12·03, 12·2, 11·91, 12·02, 12·00, 12·1, 12·10 per cent.

In order to show that the tin present did not interfere with the titration I treated a mixture of 0·0800 grm. of antimony and 1·92 grm. of tin in the same way. In this case the large amount of white solid ("metastannic acid"?) took about 3 hours to dissolve completely in the hydrochloric acid subsequently added. The amount of antimony recovered was 0·0795 grm.

In conclusion, it may be as well to state that I have never noticed any tendency of the perchloric acid to explode under the conditions given above. Solution proceeds quite smoothly and normally, except for the formation of stannic chloride mentioned above. The concentration of the perchloric acid appears to play a considerable part in the rate of solution, which becomes rapid only when the acid is concentrated; this is the reason for the initial heating of the acid mixture, as it is undesirable to concentrate the acid to any great extent in presence of the sample, owing to the formation of the volatile stannic or antimonic chloride. Attempts were made to eliminate the condenser altogether in the determination of antimony, but this yielded low results.

Determination of the Sulphate Ion by Precipitation as Barium Sulphate

By J. NEWTON FRIEND, D.Sc., F.I.C., and W. N. WHEAT, B.Sc.

Apparently Fresenius (*Z. anal. Chem.*, 1870, **9**, 52) was the first to direct attention to the fact that barium sulphate, upon precipitation from solution, tends to carry down with it appreciable quantities of dissolved substances. This is particularly the case if barium chloride is used as the precipitant when determining the sulphate ion of salts of alkali metals. The occluded matter may then consist of barium chloride or alkali sulphate according to circumstances; if the former, the results are too high; but if the latter, they are too low (Allen and Johnston, *J. Amer. Chem. Soc.*, 1910, **32**, 588; Karaoglanov, *Z. anal. Chem.*, 1917, **56**, 417; Kolthoff and Vogelenzang, *Pharm. Weekblad*, 1919, **56**, 122). Röhrig (*J. pr. Chem.*, 1888, **37**, 225) was the first to record the absorption of lithium sulphate, and one of us (*J. Chem. Soc.*, 1929, 2330) found that the results with this salt may be several units per cent. in error. Being desirous of obtaining, if possible, accurate determinations of lithium sulphate we began this investigation.

Considerable difference of opinion has been expressed as to the manner in which impurities are retained by barium sulphate. Some attribute it to the formation of compounds such as $(BaCl)_2SO_4$ (Patten, *J. Amer. Chem. Soc.*, 1903, **25**, 186; Hulett and Duschak, *Z. anorg. Chem.*, 1904, **40**, 196), $K_2Ba(SO_4)_2$ (Kolthoff and Vogelenzang, *loc. cit.*) and $K_2[Ba_5(SO_4)_6]$ which Balareff (*Z. anorg. Chem.*, 1922, **123**, 69) claimed to have isolated. Others have suggested solid solution, the first to do so being Schneider (*Z. physikal. Chem.*, 1892, **10**, 425). Korte (*Trans. Chem. Soc.*, 1905, **87**, 1503), however, decided against this, and concluded that the action is partly chemical and partly physical, as previously suggested by Richards (*Z. anorg. Chem.*, 1902, **25**, 220). Many investigators now favour adsorption

(Weiser, *J. physical Chem.*, 1917, **21**, 214; Karaoglanov, *Z. anal. Chem.*, 1917, **56**, 225, 417; Chakravarti and Dhar, *Kolloid-Z.*, 1928, **44**, 63, and Balareff, *Z. anal. Chem.*, 1927, **72**, 303), a view that receives support from the electro-osmotic measurements of Mukerjee and Basü (*J. Indian Chem. Soc.*, 1926, **3**, 371), and from the observed general adsorptive power of precipitated barium sulphate (see de Brouckere, *Bull. Soc. chim., Belg.*, 1929, **38**, 409; 1930, **39**, 174). Further, microscopic examination shows that precipitated barium sulphate possesses fine capillaries, and adsorption of barium chloride in these may be so complete that a porous pot, in the pores of which barium sulphate has been precipitated, can function as a semi-permeable membrane with respect to solutions of barium chloride (Balareff and Kandilarov, *Z. anorg. Chem.*, 1927, **162**, 344). We have adopted the theory of adsorption as our guiding principle.

Two methods have already been recommended for making fairly accurate determinations of alkali sulphates. According to one (Richards and Parker, *Z. anorg. Chem.*, 1895, **8**, 413), excess of barium chloride is added, whereby the whole of the sulphate ion is precipitated as barium sulphate, the precipitate being contaminated only with barium chloride. After the precipitate has been ignited and weighed in the usual way the chloride is determined by fusion of the whole with sodium carbonate and determination as silver chloride. The equivalent amount of barium chloride is subtracted from the original precipitate, and the true amount of barium sulphate is obtained. This is too cumbersome for ordinary procedure. A second method consists in precipitating as barium sulphate under standard conditions and applying an empirical correction (Winkler, *Z. angew. Chem.*, 1920, **33**, 59, 159, 162; Allen and Johnston, *J. Amer. Chem. Soc.*, 1910, **32**, 588). The principle of this method cannot be regarded as satisfactory.

Adopting the view that contamination of the precipitate is due essentially to adsorption, we hoped it might be possible to remove adsorbed material by a simpler method than that of Richards and Parker by modifying the conditions in accordance with recognised principles for avoiding adsorption in general.

As theory demands, adsorption by barium sulphate is reduced by precipitation in extremely dilute solution (Hahn and Otto, *Z. anorg. Chem.*, 1923, **126**, 257), whilst prolonged standing is found to reduce the amount of adsorbed alkali sulphate (Allen and Johnston, *loc. cit.*; Johnston and Adams, *J. Amer. Chem. Soc.*, 1911, **33**, 829). When precipitated very slowly at 100° C. barium sulphate may be obtained very free from contamination by using a diffusion method extending over several days (Johnston and Adams, *loc. cit.*).

We find that very satisfactory results can be obtained with lithium sulphate in solutions containing no other dissolved substances by adopting the following precautions:

(1) The concentration of the alkali sulphate should not exceed about 0·01 grm.-mol. per litre.

(2) The solution—conveniently about 350 c.c.—is acidified with hydrochloric acid, the concentration of which is best kept near $N/100$, since barium sulphate is appreciably soluble, even in dilute acid (Sjollema and van't Kruys, *Chem. Weekblad*, 1907, **4**, 589; Jensen, ANALYST, 1928, **53**, 136).

(3) The solution is now heated to boiling, and a dilute solution of barium chloride is added dropwise, with constant stirring, until about twice the amount of barium chloride theoretically necessary for precipitation has been added. This ensures complete precipitation of all the sulphate ion (see Richards and Parker, *loc. cit.*). The low results in experiments 15 to 18 (see Table) are in part attributable to insufficient excess (10 per cent.) of barium chloride.

(4) The solution is kept near the boiling-point for ten minutes and is then allowed to stand over-night. Immediate filtration was found to yield somewhat erratic results, probably because equilibrium had not been established. Sometimes the weight of precipitate was greater upon immediate filtration than upon standing (expts. 5, 6), but usually less (expts. 7 to 10, 11 to 14, and 15 to 18), probably in part because of the greater solubility of the precipitate in hot than in cold solution, for the liquid that had stood for some time was always filtered cold.

No.	Volume of solution c.c.	Normality of HCl	Excess of BaCl$_2$ added Per Cent.	Duration of standing before filtration Days	Nature of filtration	Anhydrous lithium sulphate		Error Per Cent.
						Taken Grm.	Found Grm.	
1	200	*N*/100	100	1	Cold	0·2688	0·2701	+0·48
2	"	"	"	5	"		0·2689	+0·04
3	200	2*N*	100	1	Cold		0·2687	−0·04
4	"	"	"	5	"		0·2702	+0·52
5	400	*N*/10	100	Nil	Hot		0·2698	+0·37
6	"	"	"	6	Cold		0·2688	0·00
7	200	*N*	100	Nil	Hot		0·2660	−1·04
8	"	"	"	Nil	"		0·2633	−2·04
9	"	"	"	14	Cold		0·2716	+1·04
10	"	"	"	14	"		0·2706	+0·67
11	100	*N*	120	Nil	Hot	0·3935	0·3959	+0·61
12	"	"	"	Nil	"		0·3962	+0·69
13	"	"	"	14	Cold		0·3976	+1·04
14	"	"	"	14	"		0·3985	+1·27
15	400	*N*/10	10	Nil	Hot		0·3782	−3·89
16	"	"	"	Nil	"		0·3805	−3·31
17	"	"	"	1	Cold		0·3858	−1·96
18	"	"	"	1	"		0·3856	−2·01
19	350	*N*/100	100	1	Cold*	0·3875	0·3885	+0·26
20	"	"	"	1	" *		0·3893	+0·46
21	350	*N*/20	100	1	Cold	0·3875	0·3872	−0·08
22	"	"	"	1	"		0·3874	−0·03
23	350	*N*/100	100	1	Cold		0·3873	−0·05
24	"	"	"	1	"		0·3879	+0·10
25	"	"	"	1	"		0·3874	−0·03
26	"	"	"	1	"	0·3552	0·3548	−0·11
27	"	"	"	1	"		0·3552	0·00

* 40 minutes' heating only (p. 562)

(5) After standing, the clear, supernatant liquid is decanted through a filter as completely as possible, some 350 c.c. of distilled water are added to the barium sulphate, and the whole is heated for not less than two hours in a water-bath, with frequent stirring. This process, which serves to remove most of the remaining

adsorbed material, was not done in expts. 1 to 18. Expts. 19 and 20 indicate that 40 minutes' heating is insufficient for this purpose. The solution is now cooled, the supernatant liquid is filtered off, and the precipitate is washed into the filter with a minimum quantity of hot water. By filtering in the cold, any correction for the solubility of barium sulphate is rendered negligibly small.

(6) The filter paper is dried, the precipitate is detached and transferred as completely as possible to a porcelain (not platinum) crucible, the paper being incinerated separately and the ash arranged on one side of the crucible. After the ignition a drop of dilute sulphuric acid is added before the final heating and weighing (Acree, *J. Biol. Chem.*, 1906, 2, 135; Pellet, *Ann. Chim. Anal.*, 1907, 12, 186, 318; Truchot, *ibid.*, 1907, 12, 267; Folin, *J. Biol. Chem.*, 1907, 3, 83).

The results obtained in this investigation are summarised in the table. Expts. 21 onwards were carried out according to the method outlined above. Spectroscopic examination of the ignited precipitates showed that traces of the alkali metals were still present. Nevertheless, the results are as concordant as is usually required in ordinary quantitative analysis.

We desire to thank Mr. R. H. Vallance for carrying out some analyses to check the above results.

THE TECHNICAL COLLEGE,
BIRMINGHAM

The Water-Protein Ratio of Lean Meat, and Its Bearing upon the Analysis of Sausages

BY F. W. JACKSON, B.Sc., A.I.C., AND OSMAN JONES, F.I.C.

(*Read at the Meeting, April* 6, 1932)

THE Meat Rationing Order, 1918, (No. 404) of the Ministry of Food, fixed the minimum quantity of meat in sausages as 67 per cent. for first quality and 50 per cent. for second quality. When the Order came into force it was necessary for analysts to employ some suitable method for the determination of the percentage of meat in sausages, a point which hitherto had received little attention.

In the ANALYST for April, 1919 (44, 125, 127), two methods were published, one by George Stubbs and Andrew More, and the other by A. W. Stokes. Both methods were based upon the average percentage of water and nitrogen in de-fatted meat. Stokes assumed that all meat contained on the average 70 per cent. of water, and based his calculations upon this figure. Stubbs and More worked upon varying water-protein ratios for de-fatted meat according to the kind present. For pork they used 3:1; for beef, 3·26:1; and for mixed meats, 3·13:1.

According to Moulton (*Meats through the Microscope*, University of Chicago Press, pp. 320, 321) the water-protein ratio for the composite lean flesh of pork (118 samples) is 3·4:1, and for composite beef flesh (34 samples) it is 3·6:1. The figures show that the water-protein ratio varies, not only for different kinds of meat, but also for different "cuts" of the same meat.

We obtained the following figures in the analysis of samples of meat, which may be regarded as representing the average quality used by reputable manufacturers of sausages.

TABLE I

SAMPLES OF PORK

As much as possible of the external fat was removed prior to the analysis of the samples, so that the samples can be regarded as lean meat as commonly used in sausage manufacture.

Description of sample	Fat Per Cent.	Mineral matter and undetermined substances Per Cent.	Water Per Cent.	Protein (N × 6·25) Per Cent.	Water-protein ratio
Gammon	2·87	1·05	73·97	22·11	3·35:1
Gammon	5·01	1·23	72·20	21·56	3·37:1
Gammon	9·21	1·33	68·78	20·68	3·32:1
Gammon	3·41	1·20	73·08	22·31	3·28:1
Back	10·19	1·10	69·59	19·12	3·43:1
Back	26·23	1·30	55·33	17·14	3·17:1
Back	6·18	1·52	69·11	23·19	2·98:1
Shoulder	26·00	1·08	58·42	14·50	4·09:1
Shoulder	43·36	1·27	41·81	13·56	3·08:1
Shoulder	2·18	1·07	75·66	21·09	3·59:1
Shoulder	7·49	1·21	68·87	22·44	3·07:1
Mixed	1·46	1·34	75·90	21·31	3·56:
Mixed	2·86	1·18	73·40	22·56	3·25:
Mixed	5·52	1·26	74·40	18·82	3·95:
Mixed	4·39	·43	72·84	21·34	3·42:
Mixed	4·80	1·56	73·77	19·87	3·71:
Mixed	2·36	1·51	76·06	20·07	3·79:
Mixed	—	—	75·32	21·83	3·45:1
Mixed	—	—	76·66	19·93	3·85:1
Mixed	—	—	75·11	20·25	3·71:1
Mixed	—	—	77·68	20·06	3·87:1

Average water-protein ratio .. 3·4:1

SAMPLES OF BEEF

As much as possible of the external fat was removed prior to the analysis of the samples, so that the samples can be regarded as lean meat as commonly used in sausage manufacture.

Description of sample	Fat Per Cent.	Mineral matter and undetermined substances Per Cent.	Water Per Cent.	Protein (N × 6·25) Per Cent.	Water-protein ratio
Bull.					
Round	0·69	1·96	75·34	21·91	3·44:1
Flank	2·04	1·02	75·92	21·02	3·62:1
Shoulder ..	1·08	0·95	76·68	21·29	3·60:1
Shoulder	2·01	0·97	75·31	21·71	3·47:1

TABLE I—SAMPLES OF BEEF—*continued*

Description of sample	Fat Per Cent.	Mineral matter and undetermined substances Per Cent.	Water Per Cent.	Protein (N × 6·25) Per Cent.	Water-protein ratio
Bullock.					
Flat rib	5·21	0·90	73·79	20·10	3·67:1
Shoulder ..	11·05	0·80	68·93	19·22	3·59:1
Sticking—					
neck end ..	3·02	0·89	76·03	20·06	3·79:1
shoulder end ..	3·02	1·44	76·40	19·14	3·99:1
centre	4·76	0·91	74·01	20·32	3·64:1
neck end ..	2·05	0·91	76·99	20·05	3·84:1
Mixed	1·31	1·08	75·96	21·75	3·49:1
Clod	—	—	76·97	19·75	3·90:1
Flank	—	—	68·84	20·71	3·30:1
Veal	2·20	1·22	76·80	20·78	3·70:1

Average water-protein ratio .. 3·6:1

SAMPLES OF PORK (FAT)

The samples can be regarded as "fat" as commonly used in sausage manufacture.

Description of sample	Fat Per Cent.	Mineral matter and undetermined substances Per Cent.	Water Per Cent.	Protein (N × 6·25) Per Cent.	Water-protein ratio
Gammon	89·87	0·08	8·34	1·71	4·80:1
Gammon	93·32	0·07	4·86	1·75	2·70:1
Back	92·75	0·10	5·72	1·43	4·00:1
Back	93·48	0·06	5·53	0·93	5·94:1
Shoulder	90·73	0·12	8·10	1·05	7·71:1
Shoulder	90·50	0·09	7·08	2·43	2·91:1

Average water-protein ratio .. 4·2:1

It should be observed that the average figures closely approximate to those given by Moulton (*vide supra*).

We have found that the water-protein ratio varies in individual carcases. It is obviously impossible to establish an average water-protein ratio which will cover all classes of meat, such as offal, cured meats, pickings and canned meats, as well as the better-class "cuts." Indeed, it is not necessary because, with the possible exception of the very cheapest grade of sausages, manufacturers in this country have other outlets for odds and ends of meat.

An examination of the data given in Table I leads to the conclusion that the various water-protein ratios used by Stubbs and More need some modification, and that more accurate ratios would be:

Water-protein for fresh pork .. 3·4 : 1
Water-protein for fresh beef .. .. 3·6 : 1
Water-protein for fresh mixed meats 3·5 : 1

Since in most cases the analyst will not know the kind of meat which has been used in the article which he has under examination, he will of necessity have to adopt the mixed meat ratio of 3·5 : 1. It is only in special cases that the other ratios will be applicable.

When canned meat is re-canned after being mixed with other materials, as is sometimes done, the water-protein ratio may vary within such wide limits that it is not desirable to base the analysis of such a mixture upon the scheme now under discussion.

As no regulations at present exist in this country governing the meat percentage in sausages (the Meat Rationing Order, 1918, No. 404, having lapsed after July, 1920), it is probable that the determination of the amount of this product in such articles is not so important as at one time, but it is nevertheless of considerable importance to those engaged in fulfilling the conditions laid down in government and public institution contracts.[*]

It must be admitted that the *accurate* determination of the percentage composition of such articles as sausages is not practically possible at the present time; such factors as the varying water-protein ratio in meats, the kind and age of the meat used, the nature of the "filler," the nitrogen content of the "filler," the water associated with the filler, and the amount of "added water," all tend to render the final result inexact, but we feel that a nearer approximation to the correct composition of meat and cereal mixtures, such as sausages, will be obtained by using the modified water-protein ratios suggested.

The data given in Table II refer to samples of sausages of known recipe, and show the percentage of meat, as determined by the use of Stubbs and More's water-protein ratio and of the new ratios now proposed.

If reference be made to our data given in Table I, it will be observed that the ratios for fat are more variable than those for lean meat, and were it possible to eliminate some, or all, of the other errors which inevitably arise in the examination of sausages (see above), it would be necessary to take into consideration this variable ratio; but, unless the percentage of fat is abnormally high, the correction

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[*] Regulations regarding the composition of sausages in some foreign countries and British Possessions are as follows:

Holland	Sausages to be labelled with statement showing the percentage composition.
Belgium	Starch not to exceed more than 5 to 8 per cent. No statement is made with regard to percentage of added water.
Brazil	No cereal matter allowed.
France	Meat content is not fixed, but no offal may be used, and the water must not exceed 75 per cent. of the fat-free product.
U.S.A.	Sausages shall not contain cereal in excess of 2·0 per cent.
Canada	Not more than 60 per cent. of water or 5 per cent. of cereals. There must be no added water.
N.S. Wales S. Australia Tasmania Queensland Victoria N. Zealand S. Africa Straits Settlement	75 per cent. of meat. Not more than 6 per cent. of starch.

which would need to be applied would have no material effect upon the accuracy of the calculated results.

TABLE II

PORK SAUSAGES	Percentage of meat as calculated on Stubbs and More's water-protein ratio 3·0:1		Percentage of meat as calculated upon water-protein ratio 3·4:1		Percentage of meat according to recipe	
Sample No. 1	Lean meat ..	33·0	Lean meat ..	36·7	Lean meat ..	49·5
	Fat	29·8	Fat	29·8	Fat	16·2
	Total meat ..	62·8	Total meat ..	66·5	Total meat ..	65·7
Sample No. 2	Lean meat ..	22·3	Lean meat ..	24·6	Lean meat ..	30·8
	Fat	26·5	Fat	26·5	Fat	19·6
	Total meat ..	48·8	Total meat .	51·1	Total meat ..	50·4
Sample No. 3	Lean meat ..	36·8	Lean meat ..	40·3	Lean meat ..	44·8
	Fat	23·4	Fat	23·4	Fat	21·0
	Total meat ..	60·2	Total meat ..	63·7	Total meat ..	65·8
Sample No. 4	Lean meat ..	41·8	Lean meat ..	45·9	Lean meat ..	50·4
	Fat	22·8	Fat	22·8	Fat	21·0
	Total meat ..	64·6	Total meat ..	68·7	Total meat ..	71·4
BEEF SAUSAGES	Water-protein ratio 3·26:1		Water-protein ratio 3·6:1		Recipe	
	Lean meat ..	21·9	Lean meat ..	23·6	Lean meat ..	30·5
	Fat	26·6	Fat	26·6	Fat	19·6
	Total meat ..	48·5	Total meat ..	50·2	Total meat ..	50·1
MIXED MEAT SAUSAGES	Water-protein ratio 3·13:1		Water-protein ratio 3·5:1		Recipe	
	Lean meat ..	35·4	Lean meat ..	38·5	Lean meat ..	39·1
	Fat	19·8	Fat	19·8	Fat	19·6
	Total meat ..	55·2	Total meat ..	58·3	Total meat ..	58·7

Note.—In practice the so-called "lean" meat always contains a considerable amount of fat, and the fat meat some water and connective tissue, so that it is not possible for the analytical findings for lean and for fat to agree with the amounts of these substances shown by the recipe, but the total meat as determined should, of course, show a close approximation to the quantity which has been put in.

In determining the ash of the sample considerable difficulty may be experienced in removing all the carbon without using a high temperature. We have found that in some cases it is desirable to ascertain the total percentage of salt in the sample and that remaining in the ash, so that necessary adjustment can be made for the amount of salt which has volatilised at the high temperature used. Alternatively, the ignition may be conducted at a low temperature, such as that given by an Argand burner.

The practical work involved in the determination of the data given above has been considerable, and most of it has been carried out by Messrs. T. G. Joyce, B.Sc., F.I.C., H. Firth, F.I.C., J. W. Black, B.Sc., A.I.C., and B. Gough, and we are indebted to these gentlemen for the very real help given, with regard to both the work and the suggestions made.

The Determination of Meta- and Ortho-Cresols in Mixtures of Cresols

BY C. EDWARD SAGE, F.I.C., AND H. RONALD FLECK

THE preparation of synthetic resins involves the employment of phenols in large quantities, and the short range of boiling points between ortho-, meta- and para-cresols does not permit a complete separation, by commercially possible methods, of fractional distillation. In consequence of this, the meta-cresol, which is essential for satisfactory resin synthesis, is usually obtained mixed with varying proportions of its isomers.

Potter and Williams have recently suggested for the determination of ortho-cresol (*J. Soc. Chem. Ind.*, 1932, **51**, 60T) the employment of a modification of Cocking's method (ANALYST, 1920, **45**, 370), in which they make use of cineole in the reverse way to that employed for the determination of cineole in essential oils containing that substance.

Their published results indicate that they have made experiments with mixtures of cresols, and found the cineole products afford useful indications of the amount of the ortho-compound in commercial cresol, but we have carried the work a stage further by determining the freezing-points of the cineole complex with a larger range of mixtures.

The results recorded below indicate that the method is applicable to mixtures containing from 15 to 100 per cent., and that lower percentages can be estimated by mixing with an added known weight of pure ortho-cresol in the same way as Cocking determines the percentage of cineole in oils containing small proportions, by adding a known amount of cresineol and making allowance for it in calculating his results.

The method usually employed for the evaluation of cresol with respect to the meta-compound was introduced by Raschig, and has appeared in the last two editions of the German Pharmacopoeia (D.A.B.5 and 6). It involves the treatment of the cresol mixtures with sulphuric and nitric acids in order to produce tri-nitro-meta-cresol, the other cresols being oxidised and, under the conditions of the test, yielding no weighable crystalline material.

Several difficulties arise when dealing with cresol in this way, and the results of the test include very big allowances for loss during the process.

It takes a long time to perform the operations, and these are not free from danger. The cresols containing low percentages of the meta-compound yield tars and other inconvenient products, and eventually a mixture of nitro-compounds with an indefinite melting point; all of these difficulties render the method unsatisfactory.

The yield on which calculations are based is liable to considerable variation, and it is assumed, if 10 grms. of a sample of cresol yield 8·7 grms. of tri-nitro-meta-cresol, that 50 per cent. of actual meta-compound was present, these figures being far removed from the theoretical ones which might be expected when working with pure compounds.

A consideration of these facts showed the desirability of a more accurate and rapid method of estimation, and this has been worked out for mixtures of the three isomeric cresols, and it is hoped to extend the scope of the method to commercial cresylic acid. The method depends on the formation of an insoluble resin with formaldehyde in alkaline solution. It was found that ortho- and meta-cresols gave such a resin, whilst the para-compound did not.

By determination of the combined ortho- and meta-cresols in a given sample by formation of the aldehyde resins, and deducting from the result the amount of ortho-compound found by the cineole method, an approximately accurate estimate of the amount of meta-cresol can be ascertained.

The method has been verified on many mixtures of known composition, the materials used being pure cresols, the physical constants of which had been carefully ascertained.

The mean of the results of a number of determinations by means of the pure compounds has suggested a reasonably accurate factor for converting the weight of cresol resin into the weight of cresol, and this is the same for ortho- and meta-cresols. The maximum deviation experienced in obtaining this factor was ±0·1 per cent., and the mean value of the results showed that 1·33 grm. of the resin is equivalent to 1 grm. of either ortho- or meta-cresol.

The resin, obtained in the manner described hereafter, is of a pale cream colour and friable, and decomposes slowly on prolonged heating, formaldehyde vapours being evolved.

METHOD.—About 3 to 4 grms. of the cresol mixture are accurately weighed into a 50-c.c. measuring flask, and made up to the mark with a 10 per cent. aqueous solution of sodium hydroxide. The determination is made in duplicate with two portions of 10 c.c. each. These are pipetted into 100-c.c. Erlenmeyer flasks, 5 c.c. of water and 5 c.c. of 40 per cent. formaldehyde solution are added to each, and the reaction mixture is heated for exactly 5 minutes in a boiling water-bath.

The mixture is cooled and acidified with 20 c.c. of concentrated hydrochloric acid, being meanwhile vigorously shaken and kept cool. The large excess of hydrochloric acid is necessary in order to obtain the condensation product in an easily filterable form. The mixture is allowed to stand for about two hours at room temperature, then filtered on to a Gooch crucible, or on counterpoised filter papers. The resin is washed with cold water until free from chlorides, after which it is dried for exactly one hour in a water oven at 98° to 100° C., and then allowed to stand over concentrated sulphuric acid in a desiccator. The drying at 100° C. must not be prolonged, as the precipitate has a tendency to decompose.

The weight of resin, multiplied by 0·752, gives the weight of ortho- and meta-cresols in the mixture, and when the amount of ortho-cresol, found by the freezing-point method, is subtracted from the total, the remainder will be the amount of meta-cresol. The mean of two determinations should be taken.

Freezing-Point Method.—The mixed cresols (2·1 grms.) are placed in the inner tube of a standard crystallising-point apparatus. Into this is weighed 3 grms. of pure cineole, the mixture is stirred, and the freezing-point is taken when the temperature of the mixture just remains constant. The crystals are re-melted, and the freezing-point observed several times. The mean value of the results is taken after omitting the first result, which is usually low.

The standard mixtures of ortho-cresol used were prepared from the pure substance, pure meta- and para-cresol being used as the diluent. If the ortho-cresol is low in amount, the mixture can be enriched with a known weight of ortho-cresol, and allowance made for this.

Table I

Taken				Found		
m-Cresol Per Cent.	*o*-Cresol Per Cent.	Freezing-point °C.	Weight of resin from 1 grm. of mixture Grm.	*m*-Cresol Per Cent.	*o*-Cresol Per Cent.	Error Per Cent.
45·6	40·5	29·8	1·0193	45·1	40·8	−1
29·8	39·2	28·5	0·9177	29·5	39·5	−1
30·0	62·0	40·0	1·2236	30·2	62·0	+0·7
39·8	30·6	24·0	0·9363	39·7	30·6	−0·3
52·2	29·0	22·5	1·0800	52·3	28·7	+0·2

If no other phenols are present, the difference may be taken to be para-cresol.

Table II

Standard mixtures of ortho-cresol with meta- and para-cresols

o-Cresol, per cent.	100	95	90	85	80	75	70	65	60	55	50	40	30	20
Freezing-point of the cineole compound, °C.	55·2	53·5	51·7	49·6	47·7	45·6	43·6	41·4	39·1	36·8	34·2	29·5	23·6	14·6

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

NOTES ON THE HORTVET CRYOSCOPE

The Hortvet Cryoscope may be made more practical by the introduction of the following adjustments:

(1) Leakage of Ether.—The apparatus, as supplied, allows ether vapour to escape at many points. The cork is very porous and may be treated with a thick mixture of gum and French chalk, which dries to a hard surface, effectually preventing leakage. Any similar ether-insoluble mixture would serve the purpose. Leakage between the nickel screw-cap and the body of the container is stopped by the use of several wide rubber bands. The exit tube for the ether vapour

leads into an open tube with a side-tube at the base. It is preferable to replace this with a plain tube with rubber bung fitted with inlet tube and outlet tube, the latter conveying the vapour by means of rubber tubing and glass tube to the grating of the sink. The smell of ether will then be imperceptible.

(2) METHOD OF STIRRING.—The ebonite top of the stirrer has a hole through the centre; the top is unscrewed, and a stout thread is passed through the hole, the thread being jammed as the ebonite is screwed into position. The thread passes through a stout wire ring fitted in the hole at the top of the thermometer, and on the end of the thread is tied a hinged nickel ring (such as is used in loose-leaf books). The thread is of the length most convenient for working. A steady vertical pull is obtained. The stirrer is raised at each stroke to a height sufficient to ensure complete stirring of the sample, and this point may be determined by noting the figure on the thermometer to which the top of the stirrer must be raised so that the wire ring of the stirrer reaches the surface of the liquid. When the thermometer and stirrer are removed for cleaning purposes the hinged ring is opened and attached to the ring at the top of the thermometer.

(3) PARALLAX.—The magnifying glass supplied is unnecessarily large, does not magnify greatly, and is awkward to use. This glass and the rod to which it is attached may be removed by unscrewing the nut under the wooden shelf through which the rod passes. A thermometer magnifier (Gallenkamp), consisting of a clip holding an object glass, gives a better magnification, and by a simple device parallax can be avoided. On the far lens of the object glass are placed in line, and wide apart, two small black dots, and on the near lens one black dot near the centre. The reading is taken by moving the clip on the thermometer until the three dots and the top of the mercury column are in line. A slight up or down movement of the head will throw the dots out of alignment. It is only necessary to clip this attachment to the thermometer when a reading is to be taken.

(4) ICE.—It is often a matter of difficulty to obtain a supply of ice just when it may be required. At the front of the apparatus there is a metal socket, the use of which is not explained in the literature supplied with the apparatus. This may be conveniently used to obtain the small particle of ice necessary for each experiment. The starter is placed in a narrow glass tube with sealed end and flanged top, the tube being slightly wider than the starter and containing sufficient water just to cover the hole in the side of the starter, air bubbles being excluded. When the temperature of the control thermometer falls below 0° C. the cork is removed from the socket, and the tube containing the starter (and fitted with a rubber collar to prevent loss of ether vapour) is inserted in the socket. The water is "encouraged" to freeze, as the temperature falls, by manipulating the starter at intervals. When the temperature reaches the required point the tube is taken out and the starter withdrawn by a slow firm twisting movement and quickly placed in the sample. Any excess of ice on the starter may be removed by means of a wooden mallet. Some practice is required to avoid breaking the tube when withdrawing the starter, but the tubes are easily and quickly made if this should occur.

LAG.—It is very important to tap the thermometer sufficiently long after the mercury appears to have reached its highest point, in order to obtain a correct reading.

DOUGLAS HENVILLE

THE DETECTION OF RECONSTITUTED MILK

ACTING on information that reconstituted milk was being made and sold as milk by a wholesaler in the district, an inspector visited the premises and took samples. There was a box of dried milk in the yard, together with three churns—one containing milk, one containing cream, and one containing reconstituted milk, which, according to the vendor, was to be used in making cheese. No cheese or boards, cloths, etc., for making cheese were to be found, but it was denied that reconstituted milk was being sold as milk. Samples of each on analysis gave the following figures:

	Fat Per Cent.	Solids-not-fat Per Cent.
Cream	50·2	3·9
Milk	6·98	8·25
Reconstituted milk	0·85	20·62

It was doubtful whether the sample of milk did or did not consist of reconstituted milk. According to the Dried Milk Regulations, dried skimmed or dried machine-skimmed milk is dried milk containing less than eight per cent. of milk fat. The sample of reconstituted milk was, therefore, probably made from dried skimmed milk containing between 3 and 4 per cent. of fat.

At this time two samples of milk obtained in the ordinary course of sampling were found to contain excessively high percentages of solids-not-fat, and both these samples had been supplied to the retailers by the vendor of the reconstituted milk referred to above. It was also reported from a neighbouring borough that milk containing excessively high solids-not-fat was being supplied by the same wholesaler. At this period there was a scarcity of milk. In appearance these samples could not be distinguished from natural milk; they were apparently made from dried skimmed milk by admixture with water and cream and then pasteurised.

There is the same difficulty in detecting this product as there is in the case of artificial cream. The test for nitrates might in both cases give information. If the reconstituted milk is made to contain the normal amount of fat and solids-not-fat, this test might not be made on an apparently genuine milk. A positive nitrate test given by such a milk would indicate the possibility that the sample contains reconstituted milk. D. R. Wood (ANALYST, 1932, 247) mentions a sample of unwatered milk which contained a considerable amount of nitrate. Hortvet freezing-point determinations were carried out on the samples, and the following results were obtained:

		Fat Per Cent.	Solids-not-fat Per Cent.	Acidity, as lactic acid Per Cent.	Freezing-point °C.
1	Milk from yard	6·98	8·25	0·27	—0·580
2	Retail sample A ..	3·30	9·45	0·15	—0·600
3	Retail sample B ..	3·20	9·60	0·16	—0·606
4	Reconstituted milk from yard	0·85	20·62	0·42	—1·398
5	Milk taken on delivery at the request of the wholesaler from the retailer of sample B	3·10	8·75	0·15	—0·551

All the above samples were fresh when the tests were made, so that the acidity was not due to sourness. The acidity of a reconstituted milk will depend upon the amount of dried milk used, and where the solids-not-fat of the product is high the acidity of the depression of the freezing-point will also be increased.

A. van Raalte (ANALYST, 1929, 54, 266) states that a freezing-point lower than —0·59° C. must be considered as unsatisfactory, and that the milk obtained from cows with diseased udders can have a freezing-point below —0·57° C. Monier-Williams, however (*Food Reports*, No. 22), states that "however abnormal the sample from a chemical point of view, the freezing-point seems to be almost unaffected."

Freezing-point determinations were made on solutions of dried milk of varying strengths prepared in the laboratory. The solutions were prepared by weighing the dried milk in the freezing-point tube, thoroughly mixing with warm water, cooling, and making up with water to the required weight. No. 1 was made with distilled water, and Nos. 2 and 3 with tap-water. The freezing-point of the tap-water supplied to the laboratory is —0·019° C.

	Solids-not-fat Per Cent.	Freezing-point °C.
Solution 1	8·37	—0·510
„ 2	8·83	—0·550
„ 3	9·54	—0·605

As would be expected, the depression of the freezing-point increases with the content of solids-not-fat. Reconstituted milk made from the brand of dried milk used and containing a normal content of solids-not-fat shows a normal depression of the freezing-point. A high solids-not-fat figure, together with a greater depression of the freezing-point, indicates the possible presence of reconstituted milk. A sample of milk low in solids-not-fat and showing, by a positive nitrate test and a lessened depression of the freezing-point, the presence of added water, may consist of watered milk, or reconstituted milk low in solids-not-fat. The nitrate test would not, of course, be of use in districts where the water used in the manufacture of the milk is free from nitrates.

As Section 4 of the Milk and Dairies (Amendment) Act, 1922, prohibits the sale of milk reconstituted from either dried or condensed milk, dilutions of unsweetened evaporated milk were also tested.

	Fat Per Cent.	Solids-not-fat Per Cent.	Ash Per Cent.
Evaporated milk, Brand A	9·26	22·19	1·89
„ „ „ B	9·31	22·99	1·93
„ „ „ C	9·10	22·56	2·17

		Solids-not-fat Per Cent.	Freezing-point °C.
Brand A.	Dilution 1	8·37	—0·515
	„ 2	8·90	—0·553
	„ 3	9·54	—0·596
Brand B.	„ 1	9·22	—0·573
Brand C.	„ 1	9·03	—0·624
	„ 2	9·03	—0·623

The results obtained in the case of dilutions made from Brand A and Brand B are of the same order as those obtained from the dried milk. The experiments made with two separate dilutions of Brand C show a considerably increased depression of the freezing-point. It will be noted that the analysis of this brand shows the highest percentage of ash.

Legal proceedings were taken against the vendors of the two samples of milk containing 9·45 per cent. and 9·60 per cent. of solids-not-fat, respectively. In each case the summons was dismissed without costs. In a similar case at Battersea (an account of which was published in the local press) the analysis of the milk showed normal figures. It was, however, admitted by the firm concerned that the milk was made from dried separated milk, mixed with cream and water, and homogenised. It was stated that the milk was supplied only to people who knew of what it was composed. The summons was dismissed under the Probation of Offenders Act, with two guineas costs.

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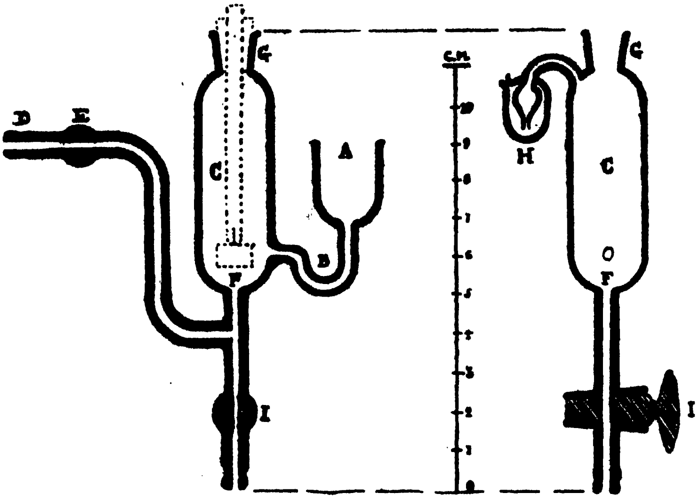
DOUGLAS HENVILLE

A HYDROGEN ELECTRODE VESSEL

Many hydrogen electrode vessels have been described, but very few of them are suitable for the rapid repetition of measurements with moderate quantities of liquid. To ensure speed in use the vessel should be made as small as is convenient, and should be totally enclosed, so that the time of saturation is short. The introduction of the liquid under examination should be possible without undue re-assembly of parts, and the solution should be removable and the vessel capable of being washed out without dismantling the electrode system.

The Clark rocking electrode (*J. Biol. Chem.*, 1915, **23**, 475) has all these advantages, but requires the use of expensive shaking apparatus and a complex junction vessel. The vessel here described and shown in the scale drawing has the advantage of simplicity.



The funnel limb, A, serves as a funnel for filling and washing out the vessel, and also as a connecting-tube for the reference half-cell. The U-bend, B, acts as a trap to prevent diffusion of the junction liquid into the main vessel, C. The hydrogen stream enters at D, is controlled by the stopcock E, and finally bubbles into the vessel at the orifice, F, which is two to three mm. in diameter. The platinum electrode is supported in the neck, G, by means of a rubber stopper, and the hydrogen escapes from the trap H. When the determination is complete, the stopcock I is opened and the liquid run away to waste. The vessel is washed out by filling the funnel, A, with water, and then flushing away by opening the stopcock, I. Saturation is usually complete in three minutes, and tests can be repeated with great rapidity. The amount of solution used for each determination is five to seven ml. Temperature measurements of the solution can be made by inserting a thermometer into the funnel, A.

The vessel has been in use in this laboratory for a considerable time, and has proved satisfactory for rapid routine determinations.

The author wishes to acknowledge the permission of Messrs. Baird & Tatlock (London), Ltd., to publish this description, and to thank Dr. Sand, of the Sir John Cass Technical Institute, for his interest in the work.

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Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

MISDESCRIPTION OF BATH SALTS

On June 21st, a tradesman was summoned, under the Merchandise Marks Act, at Woolwich Police Court for selling, under a false trade description, a packet of bath salts. Evidence was given that the defendant had sold the packet for 2d., and that its contents, when analysed, were found to consist of 97·8 per cent. of ordinary salt, with 2·2 per cent. of moisture and impurities.

The Stipendiary Magistrate (Mr. Metcalfe) said that he was satisfied that the defendant sold the salt under a false trade description. He regarded the case as very serious, and imposed a fine of 40s.

Department of Scientific and Industrial Research

FOOD INVESTIGATION

THE FREEZING, STORAGE AND TRANSPORT OF NEW ZEALAND LAMB*

The introduction to the Report deals with the scientific basis of the freezing, storage and transport of frozen mutton and lamb. Autolysis is so slow, even at the freezing-point of meat, that its effects may be ignored. Micro-organisms which can cause spoilage, either by decomposition of the flesh by the enzymes they produce, or by the absorption, particularly by the fats, of the nauseous products of their metabolism, are not very active at temperatures below freezing, and, even on frozen meats, growth is restricted almost entirely to yeasts and moulds. Probably growth ceases at about −8° C. Changes in the fat are due either to hydrolysis, in which the glycerides are partly broken down to the corresponding fatty acids and glycerol without change in flavour (Analyst, 1931, **56**, 748), or to oxidation, when lower fatty acids and aldehydes giving an unpleasant taste are produced. Both changes were very slight in carcases held at −10° C. for 18 months, and oxidation was much below that necessary to alter flavour (Analyst, 1931, **56**, 538). During storage at temperature constantly below −8° C., changes affecting the physical properties of consistence and appearance, but not, so far as is known, the dietetic value of the meat, may occur. The work on fish at the Torry Research Station (Analyst, 1931, **56**, 531) may mean that storage at much lower temperatures (−20° C.) is advisable from this point of view.

The object of the present Survey was to secure accurate data concerning temperature, relative humidity, and movement of air throughout each stage from the abattoirs in New Zealand to the wholesale markets in Great Britain, and to correlate these data with the appearance of the meat and its loss in weight. Part I deals with the analysis of the physical conditions, including cooling floors, freezing chambers, cold stores in New Zealand, and transport from stores to ship. The materials used for thermal insulation are described, and the use of self-contained refrigerating plants for rail and road vans is discussed. Overseas transport, transport from the docks to the cold stores, and a summary, with comparisons of the total losses in weight, conclude Part I.

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* Special Report No. 41, by E. Griffiths, J. R. Vickery, and N. E. Holmes. Obtainable at Adastral House, Kingsway, W.C.2. Price 7s. 6d. net.

Part II deals with the effects of environment on the quality and appearance of New Zealand mutton and lamb. It is emphasised that loss of bloom of carcases of lamb during storage is approximately proportional to the extent of the evaporation of water from them. Loss of bloom may result from an increase in the opacity of the connective tissue or skin covering the carcase owing to excessive drying of the superficial muscles, or from chemical changes of the red muscle pigment haemoglobin to the brown oxidised methaemoglobin. Such changes may be prevented or minimised by not allowing sweating in contact with the outer air; by storage at a constant temperature and high humidity at or below −8° C., and by storage at very low temperatures.

The general conclusions and recommendations of the Report include many suggestions for improvement at the various stages. It is noted that the average total loss of weight during cooling; freezing; 28 days' storage in New Zealand; ocean transport, and 28 days' storage in Great Britain, as determined for 657 carcases of prime quality, was 3·65 per cent., and was slightly greater for second-quality lamb. D. G. H.

BUILDING RESEARCH

DETERMINATION OF FREE CALCIUM OXIDE AND HYDROXIDE.*

This publication is a small-scale treatise on the determination of the calcium in calcareous building materials which is present as free oxide or hydroxide uncombined with other constituents, and reference to the original by those interested for working details of the recommended methods would be essential. The existing literature on the subject, of which a comprehensive bibliography is given, is critically surveyed. From among the varied types of methods which have been tested by the authors, the four following methods have been found to be of value in recent investigations at the Building Research Station: Lerch and Bogue's modification (*Ind. Eng. Chem.*, 1926, **18**, 739; *id.*, *Anal. Ed.*, 1930, **2**, 296) and the Building Research Department's modification of the glycerol extraction method (applicable to unhydrated cements, sand lime bricks and hydraulic lime), the lime-solution extraction method (applicable only to lime mortars and unhydrated lime), and the calorimetric method (devised for hydraulic cements and applicable to mortars and concretes). These methods, together with three methods for the qualitative detection of free lime, are described in detail, and the probable sources of errors and the accuracy obtainable are discussed.

S. G. C.

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* Special Report No. 17, by B. Bakewell and G. E. Bessey. H.M. Stationery Office, 1931, pp. 21. Price 6d. net.

Ceylon

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1931

The Government Analyst (Mr. C. T. Symons) reports that of the 2459 articles examined during the year, 1100 were in connection with 521 criminal cases. Milk adulteration was still high; of 458 samples, 262 were adulterated.

Examination of Stains.—Stained articles were examined in connection with 520 cases. Comment is made upon certain cases in which failure to take elementary precautions tended to nullify any evidence which might have been available from the scientific examination. In one instance an examination of the deposit under the finger nails for blood, etc., was required, but the prisoner had been at large for 3 days after the crime had been committed, and was then kept in custody for 5 days before being submitted for examination. In another case an exhibit, described as a "mound of earth," and said to be bloodstained, was submitted, but the "mound" had crumbled, and the analyst was expected to find bloodstains in about 20 lbs. of powdery earth.

POISONING CASES.—Poison was identified in 34 of 89 cases. Of these, 9 involved a mydriatic alkaloid (from datura, etc.), 5 arsenic (in one case with zinc chloride), 4 prussic acid, 2 each powdered glass, copper sulphate, hydrochloric acid, acetic acid, and formic acid, and one each morphine, kerosene oil, camphor, and mercury.

Powdered Glass.—Powdered glass may not be considered to be an active poison, but in one case its ingestion with rice caused considerable vomiting in two persons. In the second case a man persuaded another man's wife to introduce the powdered glass into her husband's tea, stating that it would make him of "the same way of thinking as herself."

Formic Acid as a Poison.—The appearance of formic acid in the list of poisons, in addition to acetic acid, was to be expected after its introduction as a rubber coagulant. But the use of such a strong acid in a murder case is unusual. The effects on the stomach walls were similar to those seen with acetic acid.

Prussic Acid.—In a case of prussic acid poisoning, this poison was found in the stomach, but not in the liver, kidneys, and lungs.

FIREARMS AND PROJECTILES.—Forty exhibits were examined in connection with 8 cases. In one case it was found possible to discover traces of lead in a hole in the woodwork of a chair which was said to have been caused by a bullet.

In another case 17 lead pellets and slugs were examined by spectroscopic analysis, and were found to consist of five different types of lead. The same five types of lead found in these pellets from the scene of the crime were all represented in the pellets, etc., found later with the weapon which was suspected to have been used.

The danger of drawing any definite conclusions as to the time which has elapsed since a gun was last fired was again emphasised by the results of examination of guns carried out during the year.

EXAMINATION OF DUST.—In a case of burglary, a breach was made in the wall of a house. The dust from the breach was examined and found to contain minute particles of wood such as occur where a beam of wood is affected with dry rot. Dust extracted from the garments of the suspected burglar was found to contain similar earth dust and wood particles.

SPECTROSCOPIC IDENTIFICATION OF WIRE.—The spectroscope was again instrumental in furnishing trustworthy and rapid evidence of the identity of stolen wire with Government samples.

LECTURES TO THE POLICE.—Two series of lectures were given in 1931, their object being to demonstrate to the police the possibilities arising from the scientific examination of exhibits in cases which depend largely upon circumstantial evidence. It is also hoped that they will have a beneficial effect upon the manner in which products are sent in for examination. It is a matter for regret that an increasing number of exhibits are being sent in from the courts improperly packed and labelled.

Misdescription of Articles as Spirits or Beer

FINANCE ACT, 1932

THE following notice (No. 222) has been issued by the Commissioners of Customs and Excise:—

PENALTIES UPON MISDESCRIBING ARTICLES AS SPIRITS OR BEER

I.—MISDESCRIPTION OF FORTIFIED WINES AS SPIRITS

1. *Misdescription an offence.*—Section 11 of the Finance Act, 1932, prohibits the description of any liquor in any label, wrapper, bill or advertisement of any kind, by any name or words calculated to indicate that the liquor is spirits, or a substitute for spirits, or resembles spirits, or is wine fortified or mixed with spirits, unless spirit duty has been paid on at least 97½ per cent. of the liquor.

2. *Names which amount to misdescriptions.*—A mere name amounts to a misdescription, even though in itself it may not suggest spirits, if it has in the past been used in association with any kind of statement contrary to paragraph 1. The same applies to a name similar to a name which has been so used.

3. *Sale of misdescribed liquors an offence.*—It is likewise an offence to sell or have in possession for sale any liquor misdescribed in the manner explained in paragraph 1 or paragraph 2, whether the misdescription is issued by the seller himself or by some other person.

4. *The effect.*—The effect is that it is illegal to label, advertise, sell or have in stock any liquor, which has not paid duty as spirits, under such names as "brandy wine." The same applies to fancy names which in any way suggest spirits or an admixture of spirits, and to names which are misdescriptions by association, as explained in paragraph 2. All such statements as that a liquor contains spirits, or has the flavour of or in any way resembles spirits, or is wine fortified, mixed or blended with spirits, are equally prohibited. (But see paragraph 11 as to the period of grace.)

5. *Genuine wines and cocktails.*—It is still permissible to use—(i) the recognised names of genuine wines, such as "port" or "sherry," or

(ii) cocktail names which were in use before 4th May, 1932, to describe ready-made brands of cocktails containing vermouth and spirits, the quantity of vermouth in which was at least equal to that of proof spirits.

This only applies to names, and neither wines nor cocktails may be labelled or advertised as fortified or mixed with spirits.

II.—MISDESCRIPTION OF SUBSTANCES AS BEER

6. *Misdescription an offence.*—Section 12 of the Finance Act, 1932, prohibits the description of *any substance* (*i.e.* not merely a liquor, but also, *e.g.* brewing materials in packets), in any label, wrapper, bill or advertisement of any kind, by any name or words calculated to indicate that the substance is, or is a substitute for, or resembles, *ale, beer, porter* or *stout,* unless beer duty has been paid on the whole of the substance.

7. It will therefore be illegal in future to describe liquor below the limits of 1016° in gravity and 2 per cent. in proof spirit content (unless made on licensed brewery premises and duty-paid) by any such names as "bitter ale," "herb beer," or "brown stout," or by any names including the words "ale," "beer," etc. Any words suggesting that a liquor or other substance is, or is intended for use in making, "ale," "beer," etc., will similarly be illegal. (See paragraph 11 as to the period of grace.)

8. The names "ginger beer" and "ginger ale," however, are still permissible.

9. *Sale of misdescribed substances an offence.*—It is likewise an offence to sell or have in possession for sale any substance misdescribed in the manner explained in paragraphs 6 and 7, whether the misdescription is issued by the seller himself or some other person.

III.—PENALTIES

10. The penalty for offences is a fine not exceeding £100, and forfeiture of the offending articles.

IV.—PERIOD OF GRACE

11. In both cases I and II above, up to *30th September* next inclusive is allowed as a period of grace during which goods may be sold off under the labels, wrappers, etc., under or in which they have been previously sold. This is strictly limited, however, to *labels, wrappers, cartons,* etc., *which go with the goods as sold to the public.* All window-cards, handbills and other advertisements of every kind, if contrary to the law as explained above, must be withdrawn at once.

CUSTOM HOUSE, LONDON, E.C.3
June, 1932

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis

Preservation of Milk for Determination of the Freezing-Point. Rüdiger. (*Chem. Ztg.*, 1932, **56**, 533.)—Neither potassium dichromate nor paraformaldehyde (0·07 per cent.) is recommended, as the results require a correction-factor which is not constant; β-naphthol (0·5 per cent.) is too weak in its effect. Formaldehyde (0·5 c.c. of a 5 per cent. solution in 300 c.c. of milk), mustard oil (0·1 per cent.), or mercuric chloride (0·01 per cent.) may, however, be used to preserve milk for 3 days at 25° C., the temperature-errors being 0·0055°, 0·004° and 0·002° C., respectively; the ordinary experimental error of the method is 0·003° to 0·004° C.

J. G.

Degree of Pigmentation and its Probable Relationship to the Mineral Constituents of Honey. H. A. Schuette and K. Remy. (*J. Amer. Chem. Soc.*, 1932, **54**, 2909–2913.)—Examination of a number of samples of light and of dark floral honeys shows that the former are appreciably poorer in mineral constituents than the latter. The results obtained were as follows:

		Ash	Silica	Iron	Copper	Manganese
		Per Cent.		Mgrms. per kilo		
Light	Minimum	0·04	7·20	1·20	0·14	0·17
	Average	0·06	8·90	2·40	0·29	0·30
	Maximum	0·16	11·70	4·80	0·70	0·44
Dark	Minimum	0·07	5·40	0·70	0·35	0·52
	Average	0·17	14·00	9·40	0·56	4·09
	Maximum	0·52	28·30	33·50	1·04	9·53

It is suggested that the characteristics and flavour of honey are influenced to a marked degree by the nectar and pollen, and that the honey may vary in composition and quality with the meteorological conditions to which the plants are exposed, and with the nature and fertility of the soil. The light honeys include those from alfalfa and clover, and the dark ones those from Spanish needle, tulip poplar, mint, and buckwheat. The methods of analysis are described.

T. H. P.

Accidental Presence of Acrolein in Cider-Brandy. G. Warcollier and A. Le Moal. (*Ann. Falsific.*, 1932, **25**, 271–273.)—In connection with the occurrence of acrolein in the distillates from cider and perry prepared from the last harvest, the following reactions have been investigated:—*Codeine* gave a very fugitive green colour in the presence of sulphuric acid. *Voisenet's reaction* (*Compt. rend.*, 1910, **150**, 879):—A solution of albumin in nitrous hydrochloric acid (composition not given) gave a green colour with 0·1 to 1 mgrm. per litre, and a yellow colour with larger amounts of acrolein; fairly large quantities of acetaldehyde inhibit the reaction, but traces of formaldehyde are without effect. *The Arnold–Mentzel reagent* (phenylhydrazine-hydrochloride and ferric chloride), which gives a red colour with formaldehyde, turns green in the presence of more than 1 mgrm. of acrolein. With smaller quantities a fugitive red colour, changing slowly to green, is obtained, and if the ferric chloride is omitted the reagent is more specific for acrolein, the intensity of the green colour, which develops in 12 to 24 hours, being proportional to the amount of acrolein present. If 4 c.c. of *Schiff's reagent* (a 0·025 per cent. aqueous solution of magenta decolorised with sulphur dioxide) is added to a cold mixture of about 2 mgrms. of acrolein (in 5 c.c. of solution), and 5 c.c. of 50 per cent. sulphuric acid, a stable apple-green colour develops slowly which is unaffected by small quantities of formaldehyde or acetaldehyde, and which may be matched against that produced from a standard 0·1 to 1·0 per cent. solution of acrolein in 95 per cent. alcohol. In this way 0·050 to 0·100 and 0·120 grm. per litre were found in cider and perry, respectively, and 0·120 to 1·66 and 0·625 in their respective distillates. The acrolein appears to be derived from the glycerin, and it is observed that this conversion may be brought about by micro-organisms, such as *B. amaracrylus* or *B. Welchii*, which may occur in water. J. G.

Unsaponifiable Matter of Coffee-Bean Oil. Preparation and Properties of Kahweol. R. O. Bengis and R. J. Anderson. (*J. Biol. Chem.*, 1932, **97**, 99–113.)—The first part of an investigation of the chemistry of the coffee bean is concerned with the nature and composition of the ether-soluble or fat constituents of the coffee-bean. The unsaponifiable matter represented 10 per cent. of the fat, and was a dark brown semi-solid. It is shown that the unsaponifiable fraction of the fat, extracted from freshly-roasted coffee, contains a large amount of a highly unsaturated, strongly optically active, and sensitive product, which the authors name *kahweol*, together with one or more sterols. The composition of kahweol corresponds approximately with the formula $C_{19}H_{28}O_3$. The substance apparently contains one hydroxyl group, and it melts at 143–143·5° C.; $[\alpha]_D^{21} = -204{\cdot}5°$. Catalytic reduction of kahweol yields a compound having the composition $C_{19}H_{32}O_3$, in which two hydroxyl groups are present. Reduced kahweol melts at 175° C.; $[\alpha]_D^{23} = -67{\cdot}81°$. Kahweol crystallises readily from concentrated solutions, but the form of the crystals varies with the solvent. It is very unstable; pure colourless crystals in a sealed tube filled with carbon dioxide change to a deep yellow colour in less than 24 hours. It would seem that a substance which is so sensitive, as is kahweol, to reagents, light, heat and oxygen, must possess some active physiological properties, but, so far, all tests made have given entirely negative results. A small amount of a phytosterol which was very similar to sitosterol was also isolated from the unsaponifiable fraction of the fat. Its ultimate composition corresponded with the formula $C_{27}H_{45}OH.H_2O$; it melted at 138–139° C., and had optical rotation −35·58°. P. H. P.

Colour Reactions of Novocaine (Procaine), Anaesthesine and Allied Compounds which Distinguish them from Cocaine and Similar Substances. M. Wagenaar. (*Pharm. Weekblad*, 1932, **69**, 727–737.)—The results are summarised below, and an attempt is made to correlate the reactions of these compounds towards various reagents with their structural formulae. Column (1) is Chalmot's reaction (*Amer. Chem. J.*, 1893, **15**, 276), a positive result being a violet colour on the addition of a crystal of the sample to a drop of furfuraldehyde. Column (3) is the ordinary diazo-reaction (which responds only to NH_2-groups), a positive result being indicated by a red condensation product with a dilute solution of β-naphthol in ammonia or sodium hydroxide solution. Columns (2) and (4) give the results obtained by reactions (1) and (2), respectively, after nitration and reduction, the latter (column 4) being Guerbet's reaction (ANALYST, 1920, **45**, 334; 1921, **46**, 11). The sample is evaporated with a drop of fuming nitric acid, and the nitro-compound is then reduced by the action of a few drops of a dilute solution of stannous chloride. A positive reaction is characteristic of the phenyl group. (See also Gerhardt, *Pharm. Weekblad,* 1926, **63**, 560; and Merz, *Arch. Pharm.,* 1932, **270**, 97, 125.)

Compound	1	2	3	4
Aniline	+	Not tested	+	Not tested
p-Amino benzoic acid	+	,,	+	,,
Anaesthesine	+	,,	+	,,
Novocaine (procaine)	+	,,	+	,,
Tutocaine	+	,,	+	,,
Butyne	+	,,	+	,,
Orthoform	+	,,	+	,,
Pantocaine	—	,,	—	,,
Holocaine	—	,,	—	,,
Diocaine	—	,,	—	,,
Cocaine	—	Pale yellow	—	Pale yellow
β-Eucaine	—	Yellow	—	Yellow
Stovaine	—	Pale yellow	—	Pale yellow
Alypine	—	,,	—	,,

J. G.

Determination of Santonin by means of 2:4-Dinitrophenyl-hydrazine. O. Fernandez and L. Socias. (*J. Pharm. Chim.,* 1932, **124**, 49–54.)—To determine the santonin in wormseed, 10 grms. of the powder are lixiviated with benzene for 24 hours, and, after evaporation of the extract to dryness, 50 c.c. of 15 per cent. alcohol are added to the residue. After being heated for 15 minutes beneath a reflux condenser the liquid is filtered hot, and the flask and paper are washed three times with 5 c.c. of boiling 15 per cent. alcohol. To prevent crystallisation, 85 c.c. of a solution containing 1 grm. of hydrazine in 38 c.c. of water, 38 c.c. of 95 per cent. alcohol and 10 c.c. of sulphuric acid are added. From this point onwards the method is the same as for pure santonin; the hydrazone is formed by the addition of twice the volume of a solution prepared by dissolving 1 grm. of 2:4 dinitrophenyl-hydrazine in 90 c.c. of water to which 10 c.c. of concentrated sulphuric acid have been added, and boiling and filtering, if necessary. After 48 hours' contact in a cool dark place the liquid is filtered, the precipitate is washed with a mixture of 100 c.c. of water and 50 c.c. of 95 per cent. alcohol, dried and weighed. In the case of chocolate containing santonin the fat is removed, the residue is boiled with 95 per cent. alcohol, and, after being filtered, the solution is concentrated and treated as for wormseed with aqueous hydrazine solution, alcohol, and sulphuric acid, and the determination is carried out as for pure santonin. The amounts recovered in nine experiments with pure santonin varied from 98·72 to 99·88 per cent.

D. G. H.

Detection of Antipyrine in Pyramidone. P. Duquénois. (*J. Pharm. Chim.*, 1932, **124**, 28–31.)—A modification of the Belgian Pharmacopoeia method is recommended for the rapid detection of antipyrine in pyramidone. When a few c.c. of nitric acid containing nitrous oxides are introduced below the pyramidone solution, a violet ring characteristic of pyramidone is immediately formed, whilst the acid below should be of a yellow-green colour. In the presence of antipyrine a brownish-yellow zone is formed under the violet ring, and in a short time (up to 5 minutes according to the proportion present) with a minimum of 2 per cent. of antipyrine, a green ring of nitroso-antipyrine is formed between the brown and violet zones. D. G. H.

Reduction of Molybdic Reagents by Cherry Laurel Water. F. Morvillez and Defossez. (*J. Pharm. Chim.*, 1932, **124**, 27.)—The positive Pecker's reaction (formation of a blue colour on addition of a solution of ammonium molybdate acidified with sulphuric acid) given by commercial cherry laurel water was found to be due to the constant presence of copper, the presence of tin being only accidental. D. G. H.

Biochemical

Determination of Zinc in Biological Materials. W. R. Todd and C. A. Elvehjem. (*J. Biol. Chem.*, 1932, **96**, 609–618.)—The new micro-method described, which is adapted to amounts of zinc varying from 0·1 to 2·0 mgrms., is based on the precipitation of zinc as zinc ammonium phosphate and a colorimetric determination of the phosphorus in the precipitate (by the Fiske–Subbarow method, ANALYST, 1926, **51**, 205), from which the amount of zinc is calculated. A modification of Fairhall and Richardson's method (*J. Amer. Chem. Soc.*, 1930, **52**, 938), which involves the co-precipitation of zinc with added copper as sulphides, is employed for the preliminary separation of the zinc. *Method.*—The sample is ashed. The ash is dissolved in dilute hydrochloric acid, the filtered solution is diluted to about 30 c.c., and 5 c.c. of sodium citrate solution (100 grms. of sodium citrate dissolved in 300 c.c. of water) and 2 mgrms. of copper as sulphate are added. The solution is adjusted to p_H 3·5 by adding saturated potassium hydroxide solution (brom-phenol blue as indicator), and heated to boiling, and hydrogen sulphide is passed through it until it is cool. The contents of the precipitation flask are transferred to a 50-c.c. Pyrex centrifuge tube (the flask being rinsed out with 10 c.c. of hydrogen sulphide water buffered with sodium citrate and adjusted to p_H 3·5) and centrifuged at 1500 R.P.M. for 5 minutes; the clear liquid is decanted and rejected. The precipitate of mixed zinc and copper sulphides is washed twice by centrifuging with 15-c.c. portions of the special washing solution, described above, and decanting. The precipitate is dissolved by heating it with a mixture of 3 c.c. of water and 0·5 c.c. of concentrated hydrochloric acid, 0·5 c.c. of hydrogen peroxide (30 per cent.) being added, drop by drop, to oxidise the sulphide. The solution is transferred to the original precipitation flask, evaporated to a small volume to destroy the hydrogen peroxide, and diluted to 30 c.c., the zinc and copper are re-precipitated with hydrogen sulphide at p_H 3·5, and the precipitate is dissolved as before. The solution is evaporated almost to dryness, 22 c.c. of water and 2·5 c.c. of concentrated hydrochloric acid are added, and hydrogen sulphide is passed for 5 minutes to precipitate the copper sulphide, which is separated and washed by the centrifuge method used above, dilute hydrochloric acid saturated with hydrogen sulphide being used for the washing. The solution and washings containing the zinc are evaporated nearly to dryness, and the residue is transferred to a 15 c.c. graduated centrifuge tube; the total volume should be less than 5 c.c. The p_H value is adjusted to 6·6 (brom-thymol blue as indicator), the liquid is heated to 90° C., and 0·5 c.c. of diammonium hydrogen phosphate solution (10 per cent., adjusted to p_H 8–9) is added, drop by drop. The liquid is kept for 30 minutes at 90° C. to enable the initially-formed amorphous precipitate of zinc ammonium phosphate to become crystalline, set aside for 4 hours, and then centrifuged for 5 minutes. The precipitate is washed, by centrifuging and decanting, with 5 c.c. of diammonium hydrogen phosphate solution (1 per cent., rendered faintly pink to phenolphthalein with ammonia), and then with 10 c.c. of alcohol (50 per cent.), the tube being finally left in an inverted position to drain. The precipitate is dissolved in 8 c.c. of 2 N sulphuric acid, and the solution is treated with 5 c.c. of a 2·5 per cent. solution of ammonium molybdate in 3 N sulphuric acid, and with 2 c.c. of aminonaphtholsulphonic acid solution (0·5 grm. of 1:2:4-aminonaphtholsulphonic acid dissolved in a mixture of 500 c.c. of 5 per cent. sodium bisulphite solution with 5 c.c. of 20 per cent. sodium sulphite solution). After dilution to 50 c.c. the colour developed is compared in a colorimeter with a standard prepared from 2 c.c. of a standard phosphate solution (1 c.c. = 0·1 mgrm. of phosphorus) in a similar manner, except that 5 c.c. of a 2·5 per cent. solution of ammonium molybdate in 5 N sulphuric acid are used. The zinc content is calculated from the amount of phosphorus found according to the ratio of zinc:phosphorus in $ZnNH_4PO_4$. Results are cited of test determinations of zinc in pure solutions and in a wide variety of biological materials. S. G. C.

Separation of Vitamin *A*, Carotene and Xanthophyllen. P. Karrer and K. Schopp. (*Helv. Chim. Acta*, **1932**, **15**, 745–746.)—Vitamin *A*, pro-vitamin *A*, and carotene, which often occur together in products of animal origin, like butter and egg-yolk, may be readily separated by chromatographic analysis with the help of adsorbent clay (*Fasertonerde*). A solution of the vitamin *A* and carotene in petroleum spirit is drawn down by suction through a tube filled with the clay, which is afterwards rinsed with a large quantity of petroleum spirit. The upper adsorption layers contain only vitamin *A*, and the lower ones mainly carotene, which may be completely freed from traces of the vitamin by a second adsorption. Elution of the adsorbed compounds is effected as usual with a mixture of petroleum spirit with 10 per cent. of methyl alcohol. Spectroscopic examination of the two carotinoids obtained furnishes evidence of the completeness of the separation.

For separating vitamin *A* from xanthophyll and zea-xanthine, the demixing method is inapplicable, since, in the distribution between petroleum spirit and methyl alcohol, the vitamin and the two oxygenated carotinoids pass into the alcoholic phase. Here, again, chromatographic analysis is effective. If a petroleum spirit or petroleum spirit and benzene solution of the products is filtered through a layer of precipitated calcium carbonate, the vitamin *A* passes quantitatively into the filtrate, whilst the xanthophyll and zea-xanthine are adsorbed. Doubtless the oxygen-rich carotinoids, viola-xanthine, capsanthin, and fucoxanthine would be similarly adsorbed. T. H. P.

Isolation and Identification of Vitamin *C*. W. A. Waugh and C. G. King. (*J. Biol. Chem.*, **1932, 97, 325–331.**)—Work on the chemical nature of vitamin *C* has been continued, particularly by the study of the solubility of the active material in organic solvents, leading towards its isolation by crystallisation. The authors describe (*a*) the precipitation of the active material as the lead salt, and (*b*) the isolation of a crystalline compound which is active in the prevention of scurvy in guinea-pigs. The compound (the vitamin) can be recrystallised readily from butyl alcohol, acetone, ethyl acetate, ethyl alcohol, or methyl alcohol, by the addition of petroleum spirit; the appearance of the crystals varies with different solvents. The properties of this active crystalline substance correspond with those given for the "hexuronic acid" studied by Szent-Györgyi (*Biochem. J.*, 1928, **22**, 1387; *J. Biol. Chem.*, 1931, **90**, 385) as an oxidation-reduction factor in adrenal cortex, oranges and cabbage. The two substances are believed to be identical, as previously stated by King and Waugh (*Science*, 1932, **75**, 357). The evidence from which the authors conclude that vitamin *C*, as isolated in their laboratory, is identical with the hexuronic acid studied by Szent-Györgyi and Kendall as a reducing factor in plant and animal tissues, is as follows (*i.e.* they correspond in): (*a*) natural occurrence so far as studied (the protective level of 0·5 mgrm. daily of the newly-described preparation corresponds with 0·5 mgrm. of hexuronic acid found by Szent-Györgyi in 1928 in 2 c.c. of orange juice); (*b*) oxidation by iodine and by Benedict's reagent (quantitative); (*c*) specific rotation ($[\alpha]_D^{20} = +25° \pm 1°$); (*d*) acid titration equivalent (exact for the free acid); (*e*) carbon and hydrogen combustion, for $C_6H_8O_6$; (*f*) reversible formation of a lactone and a free acid; (*g*) typical crystal forms; (*h*) solubility in a number of organic solvents; (*i*) precipitation as a lead salt; (*j*) instability toward alkalis and oxidising agents; (*k*) diffusion rate and electrical transference [McKinnis and King (*J. Biol. Chem.*, 1930, **87**, 615; ANALYST, 1930, **55**, 592)]; and (*l*) melting-point (183–185° C.). Further investigations of the two compounds are in progress. P. H. P.

Adventitious Presence of Selenium in certain Plants. Taboury. (*Compt. rend.*, 1932, **195**, 171).—It was shown earlier (*Bull. Soc. Chim.*, 1909, iv, **5**, 865) that the mineral waters of La Roche-Posay (Vienne) contain selenium in appreciable proportions. It is now found that, of the plants growing either in the discharge channel of these waters or on the wet banks of this channel, *Sium latifolium*, L. and *Pastinaca sativa*, L. contain selenium, which could not, however, be detected in *Scrofularia aquatica*, L. The procedure adopted was as follows: The air-dried plant was incinerated at the lowest sufficient temperature, in order to avoid both fusion of the ash and attack of the porcelain dishes used. The ash was treated with water and the clear solution was evaporated to dryness. The residue thus obtained was treated with 35 per cent. alcohol; the evaporated residue from this alcoholic solution was then evaporated with 5 c.c. of hydrochloric acid. Before the whole of the acid had been expelled, the mass was extracted with two quantities of water (4 c.c. in all), and the liquid treated at 100° C. with 1 c.c. of sodium bisulphite solution. After a few moments any selenium was deposited as a red precipitate. T. H. P.

Organic Analysis

Reactions and Reagents for the Detection of Organic Compounds. I. E. Eegriwe. (*Z. anal. Chem.*, 1932, 89, 121-125.)—When a small quantity of a calcium salt precipitate to be tested for tartaric acid is heated to 120° to 150° C. with a few c.c. of a solution of 0·01 grm. of gallic acid in 100 c.c. of 96 per cent. sulphuric acid, a bright blue coloration is obtained in presence of 0·1 to 1 mgrm. of tartaric acid. With diminishing amounts of the acid, the colour changes through bluish-green to yellowish-green (0·002 mgrm.). As little as 0·001 mgrm. of tartaric acid gives a yellowish-green colour if the reagent is prepared by dissolving 0·002 grm. of gallic acid in 100 c.c. of 96 per cent. sulphuric acid. The test may be applied in presence of oxalate or fluoride, but complex iron cyanides must be absent. It yields negative results with oxalic, citric, malic, succinic, formic, acetic, propionic, butyric, lactic, cinnamic, and salicylic acids, but positive results are obtained with glycollic, tartronic, glyceric, and glyoxylic acids, formaldehyde or carbohydrates.

Malic acid gives a bluish fluorescence when heated in a water-bath with a reagent made by dissolving 0·0025 grm. of β-naphthol in 100 c.c. of 96 per cent. sulphuric acid; when 1·5 c.c. of the reagent is used, 0·01 mgrm. of malic acid is detectable. Malic acid may be identified in this way in presence of citric and succinic acids, the test being made on the calcium salt precipitate or, if this is small in quantity, on a drop of its solution in dilute sulphuric acid. The reaction is not given by oxalic, tartaric, citric, succinic, cinnamic, benzoic, salicylic, acetic, or formic acid, but certain hydroxy-acids of the glycollic series give a marked or a faint (acids of the tartaric series) green fluorescence. Glycollic acid, which may occur in the calcium precipitate, gives a brownish-yellow coloration which masks the fluorescence due to the malic acid.

When heated for 15 to 25 minutes in a water-bath with 10 c.c. of a solution of 0·01 grm. of 2:7-dihydroxynaphthalene in 100 c.c. of concentrated sulphuric acid, 1 mgrm. of glycollic acid gives a deep red coloration with a violet tinge; with 2 c.c. of the reagent, 0·0002 mgrm. of the acid yields a bright pink colour. Solutions containing over 1 mgrm. of glycollic acid per drop (0·05 c.c.) must be diluted before being tested. Formic, acetic, oxalic, succinic, citric, benzoic, and salicylic acids give no coloration with this reagent, but lactic and malic acids yield a yellow solution with green fluorescence, and tartaric acid gives an olive-green or dark greenish-brown colour. Certain oxidising agents, such as persulphates, hydrogen peroxide, chlorates and chromates, gradually give a violet colour to the reagent, which by itself assumes a faint red or reddish-violet colour if left exposed to the air for some hours.

Since oxalic acid is readily reduced to glycollic acid by means of powdered magnesium and dilute sulphuric acid, it may be detected, after reduction, by the 2:7-dihydroxynaphthalene reagent. Glyoxylic acid also gives glycollic acid on reduction, and hence gives the same colour reaction as oxalic acid; it is, however, not precipitated from neutral solution by calcium sulphate solution. T. H. P.

Detection of Oxygen in Liquid Organic Compounds. T. Estreicher. (*Z. anal. Chem.*, 1932, **89**, 126–128.)—According to Wüstner (*ibid.*, 1932, **87**, 114), a liquid organic compound which dissolves iodine forms brown solutions of this halogen if it contains oxygen, or violet solutions if it is oxygen-free. It is found, however, that, for 28 per cent. of the whole number of such solvents, this rule is not obeyed. T. H. P.

Determination of Small Amounts of Ethyl Iodide. R. D. Cool. (*J. Biol. Chem.*, 1932, **97**, 47–52.)—The use of ethyl iodide in the indirect determination of cardiac output in man gives importance to methods for the determination of its vapour in air and water. For this purpose an iodate method is described in which chlorine or bromine is used to oxidise the iodide to iodate; the excess halogen is removed with phenol, and iodine is liberated from potassium iodide by the iodate, and determined by titration with thiosulphate. The procedure applicable to air samples containing vaporised ethyl iodide is as follows: The mixtures of ethyl iodide and air are collected in the 500-c.c. gas-sampling tubes previously described; 10 c.c. of chlorine water (containing approximately 0·35 per cent. of chlorine) not more than a day old, are placed in a reagent tube which is inserted into the end of one of the rubber connections on the sampling tube so that the pinch-clamp can be removed without allowing gas to escape. The reagent tubes are made of glass tubing slightly narrower than the neck of the sampling tube, with a 10-c.c. bulb blown at one end. The pinch-clamp is removed, the mouth of the reagent tube is pushed through the rubber tubing until it is 2 to 3 cm. within the glass neck of the sampling tube, and the chlorine water is allowed to run into the main body of the sampling tube, but not into the opposite neck; the walls are washed with the reagent by rotation of the tube. The contents of the reagent and sampling tubes are washed into an Erlenmeyer flask with a total of 30 to 35 c.c. of distilled water divided into at least three portions. The liquid in the flask is rotated, and 10 c.c. of 10 per cent. phenol-water mixture are added *rapidly* from a graduated cylinder. After the solution has stood for at least 20 minutes, 25 c.c. of water and 5 c.c. of 20 per cent. potassium iodide solution (prepared on the day it is to be used) are added, and the iodine liberated is titrated, at once, with 0·005 *N* sodium thiosulphate. When the yellow colour of the iodine has nearly disappeared, 5 c.c. of 0·2 per cent. starch solution are added, and the titration is continued until the solution is colourless. One c.c. of 0·005 *N* sodium thiosulphate is equivalent to 0·130 mgrm. of ethyl iodide in the original sample. When the highest analytical accuracy is required the 0·005 *N* sodium thiosulphate solution must be made with recently boiled distilled water, must not be more than 2 weeks old, and must be standardised each day. Five c.c. of approximately saturated bromine water (containing about 2·5 per cent. of bromine) may be used, instead of the 10 c.c. of chlorine water, in the above procedure, and the excess removed with 5 c.c. of aqueous 10 per cent. phenol solution. Experiments carried out to test the accuracy of the method are described. In the range of quantities of ethyl iodide dealt with in an indirect determination of cardiac output the average error was 0·011 mgrm., or 0·5 per cent. This is approximately one-third the error found by Starr and Gamble (*J. Biol. Chem.*, 1927, **71**, 509; ANALYST, 1927, **52**, 168) in their silver nitrate method, and may be held responsible for an error of only 2 to 3 per cent. in the value for cardiac output. The method described is at once directly applicable as an improvement in the analytical technique of the Starr and Gamble cardiac output method. P. H. P.

Detection and Determination of Dichloro-Ethyl Sulphide by Combustion. M. Maxim. (*Chem. Ztg.*, 1932, 56, 503.)—The usual methods for this determination (liberation of iodine from hydriodic acid followed by titration, or reduction of selenic acid to selenium, which is weighed) are not specific. Air is, therefore, drawn in succession through a wash-bottle containing potassium permanganate solution, and then over dry calcium chloride, and, finally, through a wash-bottle containing a solution of the sample in 50 c.c. of pure benzene (free from thiophen). It then passes through a glass combustion-tube maintained at red heat, and filled with broken pumice, except for a layer in the centre, 5 cm. long, which contains platinised asbestos. The emerging vapours are made to bubble through a 20 per cent. solution of barium chloride, to which 20 c.c. of perhydrol have been added, and the resulting barium sulphate is weighed; the error on 1·3 grm. of dichloro-ethyl sulphide is —0·34 to —0·59 grm. Alternatively, the contents of a gas-chamber may be drawn through a meter directly into the combustion tube. J. G.

Dichloro-ethylene as a Solvent. D. Mann. (*Chem. Ztg.*, 1932, 56, 452.)—Not only is dichloro-ethylene less inflammable than ether, but it is also preferable as an extracting solvent on account of its selectivity for certain *o*-compounds. Thus, at 20° C., 1 grm. of *o*-nitrophenol, dihydroxybenzene and hydroxy-benzoic acid dissolve in 0·9, 97·5 and 137·0 c.c. (± 0·5 c.c.), respectively, the figures for the corresponding *p*-compounds (1·0, 0·01 and 0·01 grm., respectively) being 62·5, more than 200, and more than 300 c.c. On shaking a mixture of 2 grms. each of *o*- and *p*-nitrophenols with 20 c.c. of this solvent, 95·3 per cent. of the former (m.pt. 214° C.) was recovered. The method may also be used in conjunction with steam-distillation for the separation of these isomers from the reaction-mixture obtained by the usual method of preparation. J. G.

Colorimetric Method for the Determination of Tartaric Acid. P. F. Underhill, F. I. Peterman and A. G. Krause. (*J. Pharm. Exp. Therapeutics*, 1931, 63, 351–358.)—The method described was developed for determining small quantities of tartaric acid in connection with studies in the metabolism of tartrates, and has also been applied in the rapid analysis of baking powder, etc. It depends on the fact that, whereas on acidification of a colourless solution of sodium metavanadate with acetic acid a yellow or orange colour is produced, in the presence of tartaric acid the resulting colour is red (*cf.* Mitchell, ANALYST, 1903, 28, 146). The depth of colour, which reaches a maximum in 10 minutes and thereafter fades, is dependent on the quantity of tartrate present. The reaction is given by racemic acid, but not by mesotartaric acid; none of the other fruit acids interfere. Lactic acid in high concentration yields a red colour, which fades rapidly. Oxalates alone give a rose colour with vanadate, but tests showed that mixtures of oxalate and tartrate give a colour corresponding only with the tartrate present in the mixture. In strong solution certain substances may interfere, but the quantities necessary for interference are greater than those encountered in excretions or fluids of the body. *General Method.*—To the clear colourless neutral solution to be tested, contained in a 50-c.c. Nessler tube, 1 c.c. of glacial acetic acid and 4 c.c. of sodium metavanadate solution (5 per cent.) are added, and the liquid is diluted to 50 c.c. After ten minutes the colour is compared with a range of standards, prepared at the same time, by treating different amounts of tartaric acid solution (1 mgrm. per c.c.) in the same manner. The standards should contain from nil to 2 mgrms. of tartaric acid in intervals of 0·1 to 0·2 mgrm., depending on the accuracy desired. In the range 1·0 to 2·0 mgrm. of tartaric acid it is stated to be possible, with practice, to distinguish differences of 0·1 mgrm. *Urine.*—The method has been applied to human urine and to that of the dog, rabbit, guinea pig and rat. The urine is decolorised by boiling with vegetable charcoal ("norit"), and the whole or an aliquot part of the filtered liquid, neutralised to phenolphthalein with sodium hydroxide, is used for the tartrate determination. *Faeces.*—About 2 grms. are weighed into a wide-mouthed bottle; 75 c.c. of boiling dilute trichloroacetic acid (2 per cent.) are added, the mixture is stirred until cool, diluted to 100 c.c. with the dilute trichloroacetic acid, 4 grms. of purified "norit" are added, and the mixture is stirred for 30 minutes and filtered through a dry filter paper. The solution is neutralised, and aliquot parts are taken for the tartrate determination. In test experiments tartaric acid and tartrates added to faeces were recovered with an error of 5 per cent. *Blood.*—To 5 c.c. of oxalated blood 25 c.c. of trichloroacetic acid solution (5 per cent.) are added, and the liquid is diluted to 50 c.c. After 15 minutes the liquid is filtered, the filtrate (which should be clear and colourless) is neutralised, and an aliquot part is taken for the determination. The foam which occasionally persists on the liquid in the Nessler glass may be discharged by the addition of 1 drop of ether. *Tartrate Baking Powder.*—One grm. of the baking powder is suspended in 250 c.c. of water, the residual starch is filtered off, and 1 or 2 c.c. of the filtrate is taken for the tartrate determination. The results recorded for the tartaric acid content of four samples of baking powder, obtained by this and by the A.O.A.C. (1925) method, agree fairly well. *Grape Juice.*—A mixture of 5 c.c. of grape juice, 25 c.c. of water, and 2 grms. of purified "norit" is boiled for 4 minutes and filtered, and the residue is washed. The filtrate is neutralised, diluted to 100 c.c., and aliquot parts of 2·5 and 5 c.c. are taken for the tartrate determination. The recorded results of analyses of six commercial samples, obtained by this and by the A.O.A.C. (1925) method, show, in general, good agreement. *Note.*—The purified "norit" used where specified was prepared by boiling 1 part of "norit" with 4 parts of hydrochloric acid (11 per cent.) for 15 minutes, filtering off and drying the residue, and heating it to dull redness for 30 minutes in a closed electric furnace; it is stored in an air-tight container. S. G. C.

Determination of Hemicelluloses by Oxidation with Potassium Dichromate. A. Jäger. (*Chem. Ztg.*, **1932, 56,** 570–571.)—Experiments are described which indicate that the conditions necessary in order to avoid autoreduction of the potassium dichromate during the heating process are as follows:—To a cool mixture of 10 c.c. of 8 per cent. potassium dichromate solution and 15 c.c.

of concentrated sulphuric acid (or 10 c.c. when dextrose is to be determined) are added about 5 c.c. (x c.c.) of the sample, and the whole is heated at 125° to 135° C. for 5 minutes. The solution is then cooled and, after dilution with 150 to 200 c.c. of water, the excess of potassium dichromate is titrated with 0·1 N ferrous ammonium sulphate solution (y c.c.) with a 2 per cent. solution of potassium ferricyanide as a spotting indicator. Then, from the equation:—

$$\frac{0{\cdot}8 - (y0{\cdot}00491) \times 0{\cdot}1375 \times 1000}{x}$$

the amount of hemicelluloses in grms. per litre is obtained. If it is necessary to work in greater dilution (*e.g.* when using the filtrate from α-cellulose determinations), the solution should be boiled (at 125° to 135° C.) for 10 and 15 minutes when 20 and 50 c.c. of sample, respectively, are taken (*cf.* H. Schmidt, *id.*, 1932, **56**, 273).

J. G.

Colour Reactions of Sterols. E. Montignie. (*Bull. Soc. Chim.*, 1932, **51–52**, 690.)—Evaporation of a dilute alcoholic solution of cholesterol in the presence of a few drops of an alcoholic solution of silico-tungstic acid results in the formation of a red-brown coloration. The phytosterols, stigmasterol and ergosterol give similar reactions, but the α- and β-cholesterylenes and cholestenone give only faint yellow-red colours. Oil of turpentine, cineole, terpenes, camphor and borneol give orange-red colours, and menthol, oil of lemon, abietic acid and other compounds containing several benzene nuclei (such as chrysene, phenanthrene, anthracene and naphthalene) give negative results. The reaction is specific for indene, small traces of which give a carmine-red colour. D. G. H.

Colour Reaction of Pyrrolic and Indolic Compounds. E. Montignie. (*Bull. Soc. Chim.*, 1932, **51–52**, 689–690.)—*Pyrrol.*—Eight to 10 drops of a 10 per cent. solution of selenious acid and 1 c.c. of concentrated nitric acid boiled with an aqueous solution of pyrrole yield a dark violet colour. The reaction is sensitive to 0·00004 grm. of pyrrole. *Indol* also yields a violet colour, and by this means 0·00005 grm. may be detected. With *scatoll*, on the other hand, a red colour results, but without nitric acid the colour is violet, turning to red on addition of the acid. With *tryptophan*, a citron-yellow colour is formed on heating, with or without the addition of nitric acid to the aqueous solution. D. G. H.

Detection and Estimation of Chemical Damage in Wool. P. Krais. (*J. Text. Inst.*, 1932, **23**, 144–146.)—The author maintains that damage in wool should not be assessed only on colour or chemical reactions. Corroboration by mechanical tests is essential, since it is mechanical strength and elasticity which count in practice. Furthermore, certain chemical damages may show in the amount of soluble nitrogen, but have no effect on the mechanical properties. The test for soluble nitrogen is as follows:—The sample (0·1 grm.) is kept for three days in a mixture of 8 c.c. of water, 10 c.c. of 1 per cent. hydrogen peroxide, and 2 c.c. of 0·5 N potassium hydroxide solution. The soluble nitrogen is in the form of ammonia, amino-carboxylic acids, etc., and is calculated in per cent. of the total nitrogen. In a fine undamaged wool this figure will be 4 to 5, and may rise to 32 or more in the damaged condition.

A table is given comparing the soluble nitrogen figure with breaking strength and extension for two samples of wool in the original condition; and (*a*) treated for 3 hours at 80° in 3 per cent. sodium carbonate solution; (*b*) bleached with 0·1 per cent. potassium permanganate solution containing excess of sulphuric acid, followed by sodium bisulphite and sulphuric acid; (*c*) boiled for 3 hours under a reflux condenser, with 0·2 per cent. sulphuric acid; (*d*) boiled for 10 hours with 0·5 per cent. sulphuric acid. The treated samples were rinsed and dried at the ordinary temperature.

In the case of one sample of wool, the soluble nitrogen figure was 3·42, and in the treated wools rose to 3·91, 3·77, 3·91, and 9·58, respectively. The breaking strength (dry) was 11·2 in the original sample, and in the treated samples 11·7, 10·3, 11·1, and 6·7. The breaking strength (wet) was 74 per cent. of the corresponding "dry" value, but only 48 per cent. after treatment (*a*). The extension at the breaking point rose from 38 (dry) to 64 per cent. (wet) in the original, and from 34 to 51 per cent. after treatment (*a*), but after treatment (*d*) the percentage extension rose from 3·2 (dry) to 34 (wet). Figures are also given for extension curves (dry and wet) and breaking strength in kilos. The author suggests that the test for soluble nitrogen be abandoned, and that reliance be placed exclusively on mechanical tests. R. F. I.

Inorganic Analysis

Comparison of the Reaction-Capacity towards Oxygen of Different Absorbing Materials used in Technical Gas Analysis. E. (*Chem. Ztg.*, 1932, **56**, 452.)—In order to remove all the oxygen from 100 c.c. of air, six treatments with a solution of 50 grms. of sodium hydrosulphite in 250 c.c. of water and 40 c.c. of 5:7 sodium hydroxide solution were required; five with a similar mixture in which the sodium hydroxide was replaced by 130 c.c. of 1:3 potassium hydroxide solution; five with a solution of chromous acetate in 10 per cent. sulphuric acid; and three with a mixture of equal volumes of saturated pyrogallol and potassium hydroxide solution (1:3). J. G.

Thiosulphate as an Acidimetric Standard. J. Bicskei. (*Z. anal. Chem.*, 1932, **88**, 414–417.)—Chemically pure, powdered sodium thiosulphate (0·2 to 0·5 grm.) is accurately weighed and dissolved in a little water. The solution is treated with 2 c.c. of 4 per cent. potassium iodate solution, 0·3 grm. of potassium iodide and 2 c.c. of starch solution, diluted to 50 to 100 c.c., and titrated to the blue end-point with the acid to be standardised:

$$6HCl + KIO_3 + 5KI + 6Na_2S_2O_3 = 6KCl + 6NaI + 3H_2O + 3Na_2S_4O_6.$$

The above quantities refer to 0·1 *N* acid; for *N* acid, tenfold quantities of thiosulphate, iodate, and iodide are prescribed. W. R. S.

Colorimetric Determination of Small Amounts of Silver. E. E. Jelley. (*J. Soc. Chem. Ind.*, **1932**, **51**, 191–193T.)—The method is based on the reduction of an ammoniacal silver solution by sodium hyposulphite (hydrosulphite) in the presence of gelatin to form a clear yellow silver solution. The following solutions are required:—(1) *Standard ammoniacal silver solution* (containing 0·1 mgrm. of silver per c.c.) prepared by diluting a mixture of 9·25 c.c. of 0·1 *N* silver nitrate solution and 25 c.c. of ammonia (sp.gr. 0·88) to 1 litre with copper-free water, *i.e.* water which gives no yellow coloration with sodium diethyldithiocarbamate reagent (*cf.* ANALYST, 1929, 54, 652; 1932, 495); this solution keeps well; (2) *Ammoniacal gelatin solution*, prepared by dissolving 2 grms. of "de-ashed" gelatin in water, adding 100 c.c. of ammonia (sp.gr. 0·88), and diluting to 1 litre (if ordinary gelatin is used, 0·2 grm. of ammonium phosphate should be added to precipitate any calcium or magnesium which it may contain). *Method.*—To the strongly-ammoniacal solution containing the silver (up to 1 mgrm.) to be determined, are added 10 c.c. of the ammoniacal gelatin solution and 0·4 grm. of sodium hyposulphite, and the volume is adjusted to 50 c.c. by the addition of approximately *N* ammonia. After thorough mixing, the liquid is warmed to 50° C. The quantity of the standard silver solution required to produce approximately the same depth of colour is treated similarly, and the colorimetric comparison is made with a Kober colorimeter. The colour fades after several hours, but satisfactory results were obtained in test experiments up to one hour after preparation. Copper, cobalt, nickel and cadmium interfere, and must be separated. The method described is to add an excess of bromine water and hydrobromic acid to the solution, which is evaporated until the silver bromide forms a coherent deposit; the precipitate is collected in a sintered glass crucible, washed with water, and the silver bromide dissolved in ammonia for the colorimetric determination. The silver content of silver and silver sulphide sols may be determined by adding bromine water to convert the silver into bromide, followed by a few drops of sodium sulphite, and then rendering the solution ammoniacal; calcium and magnesium, if present, should first be precipitated by the addition of ammonium phosphate. S. G. C.

Solubility of Antimonious and Stannic Sulphides in Ammonia and Ammonium Carbonate. P. A. Epik. (*Z. anal. Chem.*, 1932, 89, 17-23.)—A familiar procedure for the qualitative separation of arsenic from tin and antimony is based on the differential solubility of the sulphides in ammonia and ammonium carbonate solutions. The author, investigating the solubility of antimonious and of stannic sulphides in these solutions, found that ammonia dissolves considerable quantities of the two sulphides, especially on warming. Antimonious sulphide is practically insoluble in ammonium carbonate solution, whilst stannic sulphide shows a solubility of 0·17 grm. per 100 c.c. of the saturated solution. According to the experimental evidence, the qualitative procedure under discussion is not sound, and its use should be discouraged. W. R. S.

Determination of Carbon Disulphide in Benzene. T. Callan, J. A. R. Henderson and N. Strafford. (*J. Soc. Chem. Ind.*, 1932, 51, 193-194T.)—The interaction of carbon disulphide, diethylamine and a copper salt yields an intensely brown-coloured product which is employed as the basis of the following colorimetric method. To 1 c.c. of the benzene under test (containing less than 0·0001 grm. of carbon disulphide) contained in a narrow Nessler cylinder, 1 c.c. of diethylamine solution (1 c.c. per cent. in benzene which has been purified by "refluxing" with alcoholic potash, washing with water until free from alkali, and finally distilling), and 1 c.c. of copper acetate solution (0·03 per cent. in alcohol) are added, and the whole is diluted to 10 c.c. with alcohol. The colour developed is compared with a range of standards prepared by treating 0·25, 0·5, 0·75 and 1 c.c. of a solution of carbon disulphide in purified benzene (1 c.c. = 0·0001 grm. of carbon disulphide) in the same way; the copper acetate and the alcohol should be added to the test solution and the standards at the same time, and the mixtures kept for 20 minutes before making the final comparison. As little as one part of carbon disulphide in 1,000,000 parts of benzene can be detected. Pure thiophen gives no colour in the test. The method can be applied to the determination of carbon disulphide in such liquids as toluene, xylene, carbon tetrachloride, etc. Tests of the method in two independent laboratories gave good results. S. G. C.

Microchemical

Alkalimetric Micro Method for the Determination of Chlorine and Bromine in Organic Material. M. K. Zacherl and H. G. Krainick. (*Mikrochem.*, 1932, 11, 61–73.)—The substance is oxidised with a mixture of potassium dichromate and silver dichromate in sulphuric acid, the halogens liberated are absorbed in a standard alkaline solution containing hydrogen peroxide (perhydrol), and the resulting halogenides are titrated. *Reagents*: (1) Concentrated sulphuric acid (sp.gr. 1·84); (2) pure potassium dichromate; (3) silver dichromate, prepared by Autenrieth's method (*Ber.*, 1902, 35, 2057); (4) pure hydrogen peroxide (perhydrol); (5) sodium hydroxide and hydrochloric acid (0·01 *N* solutions), prepared by the Pregl method; (6) sodium methyl red as indicator. *Procedure*: For a substance containing chlorine the optimum weight of material is 4 to 5 mgrms.; for bromine, 5 to 6 mgrms. The substance is weighed in a weighing tube, such as that used by Lieb and Krainick (*Mikrochem.*, 1931, 9, 367), and transferred to the clean dry oxidation flask, which is similar in shape to a Kjeldahl flask, with a bulb 1·8 cm. in diameter. About 0·5 grm. of a mixture of equal parts of potassium dichromate and silver dichromate is put into the flask. The absorption tube, which has the shape of a burette and is 1·2 cm. in diameter, with a glass tap at the bottom, contains a glass spiral which fits round the glass tube leading from the oxidation flask. Thus a small volume of liquid in the absorption burette has a considerable depth, which facilitates the complete absorption of the halogens in the gas bubbling through it. Into the absorption burette 1 c.c. of perhydrol, and then 7·5 c.c. of 0·01 *N* sodium hydroxide solution from a micro burette are added. A small tap funnel with an external ground-glass joint is attached to the oxidation flask, and the side tube from the oxidation flask is passed to the bottom of the absorption liquid. Then 2 c.c. of concentrated sulphuric acid are placed in the tap funnel, the tap of which is connected with an oxygen cylinder through a washing solution of sodium bicarbonate. The oxygen is turned on, at the rate of 10 bubbles in 6 seconds (about 8 c.c. per minute), and the tap of the tap funnel is opened cautiously. The oxidation flask is lowered into the paraffin or glycerin bath, and heated for 30 minutes at 115° to 125° C., during which time the apparatus requires no attention. The top of the tap funnel is then closed, and the top of the absorption burette is opened so that its contents may run out into a quartz-glass conical flask. The absorption burette is washed three times with 4 c.c. of distilled water, a drop of methyl red is added, followed by a slight excess of 0·01 *N* hydrochloric acid, and the contents of the flask are boiled to drive off carbon dioxide. If necessary, a further drop of indicator is added, and the solution is titrated, while hot, with 0·01 *N* sodium hydroxide solution. The acidity of 1 c.c. of the perhydrol (which is usually equivalent to 0·06 to 0·16 c.c. of 0·01 *N* alkali) is subtracted from the titration value in a determination; for the calculation 1 c.c. of 0·01 *N* sodium hydroxide is equivalent to 0·3456 mgrm. of chlorine or 0·7992 mgrm. of bromine. The method gives excellent results with biological material, for which it is especially designed, and for a large number of pure compounds, including di-nitro compounds, but has not yet been adapted for very volatile liquid substances. (Complete apparatus from P. Haack, Vienna.) J. W. B.

Microchemical Reactions of Saccharin. M. Wagenaar. (*Pharm. Weekblad,* 1932, **69**, 614–618.)—Saccharin is soluble in alcohol and in 400 parts of cold water or 30 parts of boiling water, and is slightly soluble in ether, chloroform or benzene. It sublimes in small rosettes, and 0·05 mgrm. (1:100) is detectable by precipitation with a mineral acid from a solution in alkali. Silver nitrate gives dark micro-rosettes (0·02 mgrm., 1:200) on addition to a solution of the sodium salt; cadmium sulphate gives isolated prisms (0·025 mgrm., 1:200); pyridine and copper sulphate (Zwikker, ANALYST, 1931, **56**, 758) give well-defined oblong crystals; and mercuric chloride, added to a solution of saccharin in a slight excess of sodium hydroxide solution, gives prismatic crystals (0·01 mgrm., 1:300). Iodine dissolved in potassium iodide solution precipitates dark, weakly-dichroic needles, and 0·01 mgrm. (1:300) is detectable if 1 drop each of hydrochloric acid, hydrogen peroxide and a small crystal of potassium iodide are added in succession to the sample. These reactions were tested on beer and lemonade containing added saccharin, which was extracted in ether and then obtained by evaporation. J. G.

Note on the use of Sand for Centrifuging Small Precipitates. S. Stene. (*Mikrochem.*, 1932, **11**, 131–132.)—Two kinds of sand are used: (1) Purified sea-sand, in which the size of grain is less than 0·5 mm. (2) Merck's quartz-sand, washed and ignited; the grains are mostly long in shape, the greatest length being 2 to 5 mm. In micro-centrifuge tubes (pointed) about 5 grms. of sand are used, and in cylindrical tubes about 5 mm. of sand. The addition facilitates both the settling and the washing of the precipitate, but a little more washing liquid should be used. J. W. B.

Physical Methods

Radioactivity of Musts and Wines. E. Canals and A. Médaille. (*J. Pharm. Chim.*, 1932, **124**, 62–67.)—Nodon and Cuvier (*Compt. rend.*, 1928, **187**, No. 17) have stated that wines are invariably radioactive, such activity, in the case of the white and red wines studied by them, being sometimes equivalent to one-tenth of that of uranium oxide, but varying with the vineyard and the season. The wines of Roussillon had a radioactivity ranging between 0·074 and 0·129 millimicrocuries, *i.e.* much less than that given above. The modification of the

Curie electroscope, as used by Laborde and Chenéveau, was employed, but curves analogous to those given by them could not be obtained. Matured wines were less active than new wines; on the other hand, the latter appear to be more radio-active than the grapes (musts). D. G. H.

Reviews

A TEXT-BOOK OF ORGANIC CHEMISTRY. JULIUS SCHMIDT. Second English Edition. H. GORDON RULE. Pp. xxiv+843. London: Gurney & Jackson. Price 25s. net.

The fact that a new edition of this work should be required within six years of the publication of the first English edition shows that an advanced text-book on organic chemistry was not superfluous in this country. Whilst several shorter text-books might be mentioned, works of the type now under review have not been largely represented; perhaps the much-used Richter–Spielmann is the nearest approach. Cohen's excellent work is written from a different point of view; the new Schmidt-Rule is what it claims to be—a text-book. It is, however, a somewhat advanced text-book, and the user is expected to have a good working knowledge of elementary inorganic, organic and physical chemistry.

The order in which the very extensive subject-matter is arranged follows the usual lines, preliminary matters are disposed of with commendable brevity, and the general treatment is modern in type. There is an Introduction of 97 pages, and this is succeeded by three main divisions, *viz.* Aliphatic or Fatty Compounds (98–346), Carbocyclic Compounds (347–560), and Heterocyclic Compounds (561–793). Strictly speaking, heterocyclic compounds do not occupy the whole of Part III, which contains sections on Proteins (IX, 754–776), Chlorophyll and Other Plant Pigments (X, 776–790), in which some description of Carotinoids and Anthocyanins is given, and Enzymes (790–793). The Author and Subject Indexes which complete the work, are commendably full.

Considerable alterations have been made in the Introduction to this new edition; the early history of Organic Chemistry is dismissed in less than two pages, and the analysis of organic compounds and the determination of their molecular weights are only briefly described. The reviewer thoroughly approves of this procedure, as about eighty pages are thus available for the discussion of general topics before the systematic treatment of different classes of compounds.

In addition to the exposition of structure on classical lines, an account is given of the electronic theory of valency based on the views of G. N. Lewis, Lowry, Sidgwick and Sugden. This is followed by a section on Stereo-Chemistry, in which the earlier work relating to the asymmetric carbon (Le Bel, van't Hoff) and nitrogen (Pope) atoms is dealt with in a condensed manner, and methods of resolution are indicated. The few pages devoted to conditions for enantiomorphism are clear, and opportunity is taken to describe the type of optical isomerism, discovered by Christie and Kenner, which is now explained by the theory of restricted rotation (Bell and Kenyon, Turner and Le Févre, Mills, Meisenheimer). The questions of asymmetric synthesis (McKenzie, Marckwald, Rosenthaler, Bredig) and asymmetric decomposition (Cotton, S. Mitchell, Kuhn) are then discussed, and under the head of geometrical isomerism the results obtained with compounds containing doubly-linked carbon atoms and ring- or spiro-structure are briefly mentioned. Short accounts follow of the stereo-isomerism attributed to the presence of nitrogen or other atoms. It is hardly necessary to add that stereochemical matters crop up at intervals throughout the descriptive portion of the work; thus the chief reference to the Walden inversion is to be found on p. 278.

A short section of the Introduction (10 pages) is devoted to Tautomerism (Desmotropism, Dynamic Isomerism), and a classification is made of the principal systems exhibiting this phenomenon. The reader who wishes for more concrete examples may find many by use of the Subject Index.

Rather more than twenty pages are given to the physical properties of organic compounds; these are considered in the following order: colour, state of aggregation, melting point, boiling point, solubility, density, the parachor, electrical conductivity, polar properties, optical behaviour and heats of formation and combustion.

In the descriptive portion of the book, the order followed is fairly conventional, but the treatment is distinguished by reference to compounds which have acquired technical importance, or which are now prepared by more convenient methods than those adopted by their discoverers. To take a few examples, reference may be made to the synthesis of petroleum hydrocarbons and methanol, the halogen derivatives of ethane and ethylene, fermentation glycerol, tetralin, decalin, etc. One is somewhat surprised to find no reference to the hydrolysis of trichloroethylene or of dichlorovinyl ethyl ether.

Organic chemistry was originally concerned with the compounds isolated from animals and plants or produced from these substances by chemical reactions. The authors have, as far as possible, treated natural products in those sections of the work where they systematically belong. Thus, directly following on the monobasic fatty acids, there is mention of the phosphatides, whilst dihydric alcohols lead on to bases which stand in a genetic relationship to them, *e.g.* hydroxyethylamine, choline, muscarine, neurine, the polymethylenediamines and taurine. The reviewer was interested to read on page 240 that muscarine possibly has the structure $(HO)_2CH.CH_2.N(CH_3)_3OH$. The production of an optically active dihydroxy-*n*-valeric acid by the Hofmann degradation of the base, recently effected by Kögl, Duisberg and Erxleben, shows that this is not the case. (The reviewer thanks the authors of an ingenious detective novel for calling his attention to the optical activity of muscarine.)*

A section on aldehydic and ketonic alcohols (pp. 286–321) includes an account of the carbohydrates which is somewhat condensed. The reaction of acetone with certain compounds containing the group –CHOH.CHOH– should have been mentioned both here and in connection with the hydroxy-derivatives of cyclohexane. A short account of the cyanogen compounds includes mention of the isomerism of cyanuric acid and cyamelide. Among derivatives of carbonic acid, urea and thiourea are described, but the tautomerism of these compounds is treated too briefly. The ureides follow, and ten pages are given to them; this has to include an account of the purine group.

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* *The Documents in the Case.* By Dorothy L. Sayers and Robert Eustace. London: Ernest Benn Ltd., 1930.

Taking other naturally occurring products in order, we find muscone and civetone mentioned under cyclo-olefines, and the chemistry of rubber is discussed immediately afterwards. Tannins are described in connection with phenolic acids. In the 28 pages allotted to the hydro-aromatic compounds, most space is given to the terpenes and camphors; a short account of the sterols and bile acids is also given. Considering the limited space, the treatment is satisfactory.

In Part III, dealing with heterocyclic compounds, about twenty pages are given to the pyrrole group; in this way it has been possible to give a longer account of the colouring matters of leaves and blood than is usual in text-books. A further nine pages is allotted to chlorophyll at the end of the book.

Alkaloids are defined on page 663 as basic compounds of vegetable origin, in which at least one nitrogen atom forms part of a cyclic system. Over seventy pages following on the sections dealing with pyridine, quinoline and acridine are allotted to their chemistry. Only a brief account is given of the *Strychnos* alkaloids, the reader being referred to the original literature. About forty pages at the end of the book are occupied with proteins, plant pigments (including carotinoids and anthocyanins) and enzymes. These sections deal generally with matters not otherwise classified, and give an elementary account of these classes of compounds.

The reviewer has not referred at length to the descriptive portion of the work in so far as it concerns the preparation and constitution of synthetic organic substances, or to sundry theoretical questions, such as ring-strain, aromatic substitution, quinonoid structure, etc. This part of the work is very sound, and the whole book may be recommended to such as desire a good, up-to-date, rather advanced knowledge of organic chemistry. J. T. Hewitt

Adulteration and Analysis of Foods and Drugs. By J. F. Liverseege, F.I.C., Ph.C. Pp. xv+599. London: J. & A. Churchill. 1932. Price 36s.

Most Public Analysts and members of their staffs, and many other practical chemists, will quickly become enthusiastic concerning this book. It is written, by a well-known former Public Analyst, for all whose work lies in the same direction, and any of them would be proud to be its author.

It is a book conceived on a somewhat novel plan. As stated in the Preface, it gives an account of the analytical methods, research and memoranda, which have been found useful during forty-three years' experience in the Birmingham Municipal Laboratory. But the book does much more. It takes within its compass all those foods and drugs which normally come before a Public Analyst, and in systematic order surveys the official and unofficial standards and limits for each article, gives details of general composition, goes on to describe usual and unusual adulterants, and finally recommends methods of analysis which the author has found useful and satisfactory in working, and, in addition, gives many of the methods used by others. References to all important original papers are freely included. So far, the scheme of the book is on the lines of many predecessors, but here the resemblance ceases. After a foreword by Mr. N. Chamberlain, a former Minister of Health, the author gives us three chapters on the administration of the Adulteration Act, with many cogent comments. The costs of prosecutions, effects of fines, number of samples taken for analysis by various local authorities, adulteration statistics, cost of administration, laboratory costs, methods of sampling and records are discussed at some length. Under the section dealing with laboratory staffs, the author comments as follows:—(Page 9) "a public analyst's laboratory is not a suitable place for training boys who 'have done well in chemistry' at school . . . . The work is too responsible to be entrusted to partly-trained students." With this opinion the reviewer is in complete agreement. The two chapters on sampling and records contain many references to, and comments on, important appeal cases. The chapters on Public Analysts' certificates and the evidence in prosecution cases are interesting and informative, and will prove of value to all who have to carry out work under any of the Acts relating to foods. But not every reader will agree with the author when he states his belief (p. 34), that "the analytical figures relating to a sample shall be the actual determinations of the one who signs the certificate," for in these days it would be very difficult in many busy laboratories to conform to this restriction. The Fertilisers and Feeding Stuffs Act, 1926, as the author rightly comments, allows of the analysis being made by another (not necessarily a *deputy* agricultural analyst) under the supervision of the agricultural analyst.

The chapters on "general methods of analysis" and "normal mineral constituents" clear the way for a detailed discussion in the following chapters of the separate articles of foods and drugs included in this volume: the list is a long and comprehensive one, and adequately surveys the whole field. There are also valuable chapters on colouring matters, metallic impurities, preservatives, methods of calculation and the microscopy of starches. At the end of the book the section on dispensing is timely and most valuable, especially to those having to examine and report on medicines dispensed from prescriptions. A most valuable feature of the work is the summary of important prosecutions, with references, which follows the sections on each food or drug.

An Appendix of 25 pages gives information on the standardisation of volumetric apparatus, preparation of solutions, conversion and other factors, milk calculations, alcohol tables, quantities of articles recommended to be purchased for analysis under the Adulteration Act, and examples of the reports and evidence in prosecution cases, together with other interesting data. There is an index of appeal cases cited, and a general index of 20 pages. There is an error (p. 222) in the statement of the result of the case of *Grigg* v. *Smith*, as the author has pointed out since publication, and "the appeal was allowed" should be read instead of "the conviction was confirmed."

It is impossible to speak too highly of this work. The whole scheme of the book is praiseworthy, and it has been carried out in such a way as to produce a most readable, eminently practical and valuable work of reference for the laboratory and the library. In spite of the multiplication of books, this volume will be much in demand, for the author's long experience makes him a reliable guide on the matters of which he writes. The book is full of practical suggestions for making the Public Analyst a more efficient public servant, and our Society and all Public Analysts will be greatly indebted to its author. There are very few misprints. The book is well produced, and clearly printed on good paper, and because of its value one regrets that it has not been possible to issue it at a lower price.

ARNOLD R. TANKARD

QUANTITATIVE CHEMICAL ANALYSIS. By CLOWES and COLEMAN. Thirteenth Edition, Revised and Enlarged, by D. STOCKDALE, M.A., Ph.D. (Cambridge), A.I.C., and J. DEXTER, M.A., B.Sc. (London), A.I.C. Pp. xiv+605 (of which Tables 47 pp. and Index 13 pp.), 133 Illustrations and Diagrams. Twenty-ninth thousand. London: J. & A. Churchill. 1931. Price 18s. net.

This well-known work, first published in the year 1891, passed through twelve editions under the direction of the original authors, Dr. Frank Clowes and Mr. J. Bernard Coleman. The new edition has been revised by Dr. D. Stockdale, who has been mainly concerned with the inorganic portion, and Mr. J. Dexter, who is chiefly responsible for the organic parts of the book.

The revisers were confronted with a delicate task which they have discharged with great success; while preserving the admirable features and arrangement of the original work, they have exercised some judicious pruning. This has enabled them to make many important additions, without unduly enlarging the book, which they have brought thoroughly up-to-date.

The pruning has been effected by condensing the Table of Contents, thereby effecting a saving of several pages, by deleting a few of the older processes of analysis, and by avoiding repetition of details as much as possible. The numbering of paragraphs has been dispensed with; so, too, the Table of Separations, which is referred to now in the index. These and similar changes have enabled the revisers to insert many new processes and to describe new apparatus, all of which are now in use; the new edition contains thirty more pages than the last, but this addition is by no means a measure of all the fresh matter which has been added or substituted.

To decide what can be omitted always presents difficulty, and we regret, in particular, the omission from the new edition of the "Examples of Examination of Oils and Fats," pp. 424 and 425 of the last edition, and of some of the "Typical Analyses," namely, those on pp. 519–522 of the last edition. Students and analytical assistants have always found these very helpful, and, indeed, we have often thought that there is room for a book devoted entirely to these matters, which would be of the greatest assistance to both students and practitioners.

We would have welcomed the substitution of "determination" for "estimation" and "determine" for "estimate." *Estimation* is used throughout the book, except when dealing with vapour densities and molecular weights, in which cases the *determination* of these is referred to. To be consistent, *determination* should be used also in reference to *all* processes of quantitative analysis, for these operations are no less exact than those employed for the determinations of vapour densities and molecular weights. The word *estimate* is generally associated with the *approximate* cost of work to be done by the builder or plumber (who in the end we generally find exceeds his original estimate), and in chemical work its use should be limited to those processes which are not susceptible of great accuracy.

Part I is concerned with General Processes of Chemical Analysis; Section 1 deals with the Chemical Balance, weights and weighing; Section 2 with some physical determinations; Section 3 with general analytical operations. Among other new matter the chainomatic balance, alundum and Jena crucibles are described.

Part II, Section 4, deals with Simple Gravimetric Estimations; among the additions in this edition may be mentioned the determination of copper with thiocyanate, and of nickel with dimethylglyoxime, and the use of Devarda's alloy in the determination of nitrates.

Part III, Volumetric Analysis. Section 5 deals with the apparatus and its calibration; indicators; standard solutions; Section 6 with alkalimetry and acidimetry; Section 7, oxidation—reduction reactions; Section 8 with unclassed methods. Among the additions in this part are the pH ranges of indicators, the uses of standard solutions of barium hydroxide, potassium iodate and titanous chloride, the employment of internal indicators in the titration of iron with potassium dichromate, and of zinc with potassium ferrocyanide.

Part IV, Section 9 (Miscellaneous Methods of Analysis), deals with electrolytic, electrometric, spectrometric and colorimetric methods of analysis.

This is an entirely new section, and the scattered electrolytic and colorimetric operations of the former edition have been collected and dealt with as distinct processes of analysis. The measurement of p_H by indicators and by electrometric titration is dealt with in this part.

Part V is concerned with General Quantitative Analysis, and Section 10 deals with Technical Inorganic Analysis—analysis of ores, alloys, iron and steel, coal and coke, phosphatic manures, and dry assaying, and there is a very useful addition upon the sampling of ores and alloys. Section 11 is devoted to Water Analysis, collection and inspection of the samples, and discussion of the results of analysis; Section 12 treats of Technical Organic Analysis—of foods, tanning materials and soap; the analysis of milk, butter, alcoholic beverages, sugar and tea is dealt with.

Lane and Eynon's method for determining reducing sugars is added, and McNichol's and Wolff's methods for the determination of resin acids in soaps are substituted for Twitchell's process.

On page 395 the following statement occurs in connection with Gerber's method for the determination of milk fat: "As an ordinary routine process this method is the simplest and quickest, but it is well to check its results by some standard method, such as Adams." In the reviewer's personal opinion the inference which the authors wish to be drawn—that this method is lacking in accuracy—cannot be admitted, for it has again and again been proved that Gerber's process is not only rapid, but extremely accurate, provided the pipette and tubes are accurately calibrated and the details of the process duly followed. One would be pleased if there were more analytical processes like Gerber's, capable of equal accuracy and rapidity of execution.

On pages 401 and 402, dealing respectively with the detection of preservatives in milk and butter, the following passages occur:—"Certain substances are occasionally introduced into milk, more especially during hot weather, in order to prevent it from undergoing change," and in the case of butter, "If preservatives are detected, it may also be necessary to estimate the amount of boric acid which is present either as such or as borax"; it would have been an advantage if it had been stated that according to the Public Health (Preservatives, etc., in Food) Regulations, 1925, no addition of preservatives of any kind to milk or butter is permitted.

Section 13 deals with the examination of Animal and Vegetable Oils, Fats and Waxes, and an addition has been made in this edition in the examination of mineral oils and waxes.

Part VI, Section 14, is devoted to Organic Analysis; Section 15 deals with the Determination of Molecular Weights; Stepanov's method for the determination of the halogens has been added.

Part VII, Section 16 (Volumetric Estimation of Gases) includes calculation and calibration; Hempel's gas apparatus, Lunge's nitrometer; carbon dioxide by Pettenkofer's method; vapour density determinations.

Part VIII comprises tables for reference; results of typical analyses; tables of useful constants; list of common reagents, and their strengths, list of books for reference, index, factors for gravimetric analysis, antilogarithms and logarithms.

In this part there are a considerable number of changes in this edition—we have referred earlier to the omission of many of the results of typical analyses; among the additions are Clark and Lubs' table of standard buffer solutions, and W. Schloesser's table for the calibration of volumetric apparatus.

Chappuis' table of expansion of water is substituted for Kopp's, and Thiesen and Scheel's table of pressure of aqueous vapour replaces Regnault's.

The logarithm tables in this edition are printed in bolder type, which is a great advantage.

The index is considerably enlarged and is very full, but it is unfortunate that it is neither at the beginning nor at the end of the book, but is followed by fifteen pages of tables, which makes it a little difficult to find. In future editions we would suggest the avoidance of the repetition of the titles in the index (for instance, "lead" is once repeated), which makes reference more difficult, and might cause one to miss the earlier references.

The book is very free from typographical errors, but on pages 240 and 241 there are some misplacements of type, and on p. 66 there is a particularly unfortunate error, where, in dealing with the accuracy to be expected in the results of determinations, a tolerance of ±0·2 per cent. is suggested, but in the numerical example the variation from the truth is +0·21 per cent., and −0·19 per cent.

Instead of the familiar black cloth binding of the former editions, this is bound in dark blue cloth, a pleasant change, and in accord with the times, when even the masterpiece in our literature is to be had in attractive coloured bindings instead of the customary black.

The revisers, in the preface, make the modest statement: "We concluded that no major changes in arrangement were necessary, and, therefore, confined ourselves to comparatively minor alterations and additions to the text," and on the title page they describe their work as "An Intermediate Text-Book." The additions are far more important and numerous than these indications would lead one to expect, and the book in its present form even better fulfils the claim, on the title page of the previous edition, that it is "Adapted for use in the laboratories of Colleges, of Technical Institutes, and of Analysts," to all of which uses we strongly recommend this work, and wish it the world-wide acceptance enjoyed by the former editions. H. Charles L. Bloxam

The Essentials of Bacteriological Technique. By R. F. Hunwicke, B.Sc., A.I.C. Pp. 108. London: Williams & Norgate, Ltd. Price 8s. 6d. net.

Interest in the study of bacteriology has been greatly stimulated of recent years by the introduction of improved methods of food manufacture and handling, and by the public discussions which have taken place from time to time on the importance of food hygiene. So far, students of bacteriology, as apart from pathology, have almost invariably had to turn to American publications to supply their needs, frequently with unsatisfactory results. Mr. Hunwicke has given us a book, based on his own studies and experience, which can be taken as a reliable guide by students in the bacteriological laboratories of this country.

The first two chapters deal with laboratory equipment and apparatus, and each section is written in a clear, concise manner which will be of considerable help to students—many of whom, unfortunately, trouble too little about this part of the subject. On p. 18, No. 1 of the instructions for working autoclaves should, perhaps, be "See that there is sufficient water in the autoclave."

The next section deals with culture media and methods of cultivation. A sufficient number of formulae for media is given to enable the student to do practically any type of work that is required in an ordinary bacteriological laboratory. It would have been advisable, perhaps, to explain more fully why certain media should not be autoclaved, and that a percentage of the tubes of media sterilised by the intermittent method on three successive days should be incubated in order to test the efficiency of sterilisation. This chapter ends with useful directions for standardising media to the required p_H value.

The methods of cultivation and study of micro-organisms, together with the examples of typical organisms, should enable the student to proceed to the systematic detailed study of micro-organisms.

The chapter on anaerobes is quite skilfully dealt with, but the reviewer does not like the summary way in which the pyrogallol-soda method is dismissed; he has obtained excellent results with this method. In somewhat inexperienced hands the McIntosh-Fildes jar may give very unsatisfactory results, and even the author himself does not have absolute faith in it, since he suggests supplementing its use with that of pyrogallol-soda.

In the next chapter, on microscopy and staining methods, the student is not worried with a lot of unnecessary formulae, but is given the essential staining methods in a simple and straightforward manner. It is pleasing to note the author's insistence on the constant microscopic examination of cultures.

The chapter on the examination of Milk and Milk-Products appears to have been a little hastily written. It would be advisable to give the official Ministry of Health methods where available, and in future editions to embody any alterations which may have been made in the meantime. The reductase test, to which reference is made in this chapter, is used very largely in America, as well as Europe, and great store is set on it as an indicator of the keeping quality of milk. It is also found to be of great assistance, in conjunction with the fermentation test, in sorting out "gassy" milks.

In the Condensed Milk Section, p. 75, the statement that "reliance is placed on the high viscosity of the product, due to the addition of cane sugar, to prevent bacterial multiplication" is very debatable. The reason usually given is that multiplication is prevented by the concentration of the cane sugar present.

The chapter on the examination of water deals quite effectively with the methods, and a wise reference to Savage's *Bacteriology of Food and Water* will point to the student the way to follow up the work already done.

The book finishes with interesting chapters on "Meat and Canned Foods," "Vaccines, Diagnosis, Testing of Disinfectants, and Animal Inoculations."

In conclusion, Mr. Hunwicke must be congratulated on his work. The reviewer has tested many of the methods strictly according to the directions given in the book, and with very satisfactory results. He can cordially recommend the book to all students of bacteriology. J. D. ROBERTS

COLLOID CHEMISTRY—THEORETICAL AND APPLIED. By Selected International Contributors. Collected and Edited by JEROME ALEXANDER. Volume IV. Second Series of Papers on Technical Applications. Pp. 734. New York: The Chemical Catalog Company, Inc. 1932. Price $11.50.

Volume III of this series was reviewed in THE ANALYST (1932, **57**, 203). In the Preface to the present volume, Mr. Alexander states that, although in the preface to Volume I, published in 1926, there was mention of 175 promised papers, actually the four volumes contain 202.

Volume IV contains eleven papers on Carbohydrates (including Cellulose, Wood, Paper, Explosives, Sugar, Starch Products, and Sizing); Dyeing, three; Rubber, including Latex and Carbon Black, four; Plastics, three; Tanning, three; Photography, three; Coatings (including Paints, Colour Lakes, and Electro-Deposition), six; Foods, four; Laundry and Dry-Cleaning, two; Solidified Alcohol and Fire Extinguishers, two; Water Supply and Sewage Disposal, two. Thus, a very comprehensive range is presented. Well-known experts such as Samec, Mardles, Bancroft, Sheppard, Paine, Stiasny, McLaughlin, Emslander and Zakarias, to name but several, handle subjects in which they have made notable progress themselves. The world's universities and technical institutions have evidently been combed to secure the right men for the particular field under discussion.

The reviewer, being particularly interested in the subjects of foods, emulsions, proteins and wetting phenomena, has read twenty-three of the forty-two chapters with close attention, and has no hesitation in stating that the book is excellent. The subject-matter is clearly stated, and the summaries are authoritative. Unfortunately, owing, no doubt, to the difficulty of synchronising the receipt of papers from such widely separated sources, most of the papers are not really up to date. The reviewer's own paper was contributed in 1926, and was revised in

1930. The account of Tanning, contributed by Prof. H. R. Procter, does not indicate that this distinguished scientist died in 1927.

The reading of proofs has, on the whole, been good, but quite a number of errors have crept in. Thus, the sinusoid formula on p. 168 should read $y-a=b\sin(\sigma-\beta)+c\sin n(\sigma-\beta_1)$; H^- for H^+ on pp. 173 and 174; reference 44 on p. 576 gives Kolloid-Z. as volume 15 instead of 50. The index (p. 702) quotes Gibbs, and Gibbs, J. Willard; they relate to the same author. A number of minor spelling errors also occur.

It is permissible now to refer to Alexander's monumental task as covered by the four volumes. Taken together, they cover the field of academic and technical colloid chemistry more thoroughly than any other work. Their inclusion in any library devoted to technical chemistry, whatever its special aim, is essential. A veritable mine of information is presented, supported by thousands of references to the original literature, and the full author- and subject-indexes leave nothing to be desired. Editor and contributors alike are to be heartily congratulated.

William Clayton

Publications Received

The British Pharmacopoeia, 1932. Advance copy. The General Medical Council. To be published at 21s. net.

Perkin and Kipping's Organic Chemistry. Part I. By F. S. and F. B. Kipping. London: W. & R. Chambers, Ltd. Price 4s. 6d. net.

Chemistry at the Centenary (1931) Meeting of the British Association. Cambridge: W. Heffer & Sons Ltd. 1932. Price 7s 6d. net.

Chemical Engineering and Thermodynamics applied to the Cement Rotary Kiln. By Geoffrey Martin, D.Sc., F.I.C. London: Crosby, Lockwood & Son. Price 31s. 6d.

Explosives. Second Edition. Vol. III. By Arthur Marshall. London: J. & A. Churchill. 1932. Price 42s.

Ausgewählte Untersuchungsverfahren für das Chemische Laboratorium. By L. Winkler. Stuttgart: F. Enke. Price RM. 19.5 (bound).

Organic Syntheses. Vol. XII. London: Chapman & Hall. 1932. Price 10s. 6d. net.

Chemical Encyclopaedia. C. T. Kingzett. Fifth Edition. London: Baillière, Tindall & Cox. 1932. Price 40s. net.

Preparation of Pure Inorganic Substances. By E. H. Archibald. London: Chapman & Hall. Price 23s. net.

British Standard Specifications for Xyloles (No. 458). British Standards Institution, 28 Victoria Street, London, S.W.1. Price 2s. net, post free 2s. 2d.

Sand, Clays and Minerals. A Magazine devoted to Economic Minerals. Published quarterly. By A. Lewin Curtis. Chatteris. Price 5s. per annum.

Kingston's Sterling Fluctuation Tables (as Measured in Currencies on a Gold Standard). Second edition. Kingston's Translation Institute, 96, Leadenhall Street, E.C.3. Price 1s. 1d. post free.

Standard Samples, General Information. Circular No. 396 of the Bureau of Standards, U.S. Dept. of Commerce. 1932.

OCTOBER, 1932 Vol. LVII., No. 679

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS
AND OTHER ANALYTICAL CHEMISTS

Death

We deeply regret to announce the death, on June 14th, of Mr. E. R. Dovey, Government Analyst for Hong Kong.

The Chemical Assay of Thyroid Gland

By G. MIDDLETON, B.Sc., A.I.C.

(*Read at the Meeting, April* 6, 1932)

Iodine was first discovered in the thyroid gland by Baumann in 1895, and it soon became known that the physiological activity of the gland was due to an iodine compound. Thereafter the percentage of iodine was accepted as the basis of evaluation of thyroid, although it had not been proved that all of the iodine was present in the form of physiologically active compounds.

Kendall, in 1914 (*Thyroxine*, New York, 1929, p. 22) was the first to isolate from the thyroid a pure substance, thyroxine, possessing the characteristic physiological activity of the gland; the yield, however, was very small. Later, Harington (*Biochem. J.*, 1926, **20**, 293), using a more efficient method of extraction, obtained a much higher yield of thyroxine, which he showed to be β-[3:5-di-iodo-4-(3′:5′-di-iodo-4′-hydroxyphenoxy) phenyl] α-amino-propionic acid. Harington and Barger (*Biochem. J.*, 1927, **21**, 169) next synthesised it, and later Harington and Randall (*Biochem. J.*, 1929, **23**, 373) showed that the only organic iodine compounds present in the gland were thyroxine and physiologically-inactive di-iodotyrosine. As the result of these discoveries it became evident that the assay of thyroid gland should be based on thyroxine rather than on total iodine.

Thyroxine occurs in the gland in combination with protein, and is set free on prolonged boiling with alkalis. For this purpose barium hydroxide appears to be the most suitable alkali, the thyroxine being recovered both from the fraction insoluble in the alkali and from the precipitate obtained on acidification of the alkaline solution. This method, used by Harington (*loc. cit.*) for the preparation of thyroxine, is too complicated to form the basis of assay.

By the hydrolysis of thyroid with sodium hydroxide, followed by acidification, there are obtained two fractions, respectively insoluble and soluble in acid. Harington and Randall (*loc. cit.*) have produced evidence that the whole of the acid-soluble iodine is present as di-iodotyrosine, whilst the whole of the acid-insoluble iodine belongs, in all probability, to thyroxine; and they state that, "the only reasonable chemical assay of the therapeutic value of a thyroid preparation must be based on the acid-insoluble iodine and not on the total iodine-content of the material." The examination by this process of a number of commercial samples of thyroid tablets (Harington and Randall, *Quart. J. Pharm.*, 1929, **2**, 501) showed that the proportion of acid-insoluble iodine to total iodine varied between 28 and 60 per cent.

Although the evidence on which Harington and Randall base their proposed assay does not constitute strict proof that this process effects a complete separation of the thyroxine from the di-iodotyrosine, there is no doubt that a standardisation based on the acid-insoluble iodine is a definite advance on one based on the total iodine.

The assay for acid-insoluble iodine must comprise two stages: a separation of the material into acid-insoluble and acid-soluble fractions, and a determination of the iodine in the former fraction.

The known methods for the determination of the total iodine in thyroid gland are suitable for the determination of the iodine in the fractions, but the method employed for the separation of these two fractions must be adapted to the process used for the determination of the iodine.

DETERMINATION OF THE TOTAL IODINE IN THYROID GLAND.—The destruction of the organic matter may be carried out by ignition with an alkali, with or without the addition of an oxidising agent, or by igniting in a current of oxygen and collecting the iodine in alkali. The method now generally adopted for the determination of the iodine in the solution obtained is the oxidation of the iodide to iodate, addition of potassium iodide, and titration with thiosulphate—a method which has the great advantage that six equivalents of iodine are titrated for each one present in the original substance. Although the combination of alkali fusion and oxidation to iodate is employed by most workers who determine iodine in thyroid gland, the methods generally employed are subject to error. It is necessary, therefore, to consider the sources of error at each stage of the analysis.

Destruction of the Organic Matter.—For the destruction of the organic matter an oxidising agent is commonly added. Thus Baumann (*Z. physiol. Chem.*, 1898, **21**, 1) heated the material with dry caustic soda, subsequently adding sodium nitrate. Krauss (*J. Biol. Chem.*, 1915, **22**, 515) and Hunter (*J. Biol. Chem.*, 1910, **7**, 321) used a mixture of potassium and sodium carbonates with potassium nitrate. Kendall (*J. Biol. Chem.*, 1920, **43**, 161) used caustic soda with a little water, potassium nitrate being added after the water had been boiled off; and a similar method was used by Kelly and Husband (*Biochem. J.*, 1924, **18**, 251). Grützner (*Chem.-Ztg.*, 1914, **38**, 769) fused with caustic soda and sodium or barium peroxide.

As the use of an oxidising agent is very liable to cause trouble at a later stage (see below), Schulek and Stasiak (*Pharm. Zentr.*, 1928, **69**, 113) used powdered caustic potash, Smith (*Quart. J. Pharm.*, 1928, **1**, 372) powdered caustic soda, and Pickworth (*Biochem. J.*, 1925, 19, 769) a strong solution of caustic soda, which was evaporated down and ignited. In these cases no oxidising agent was added to the melt.

Methods in which a substance is evaporated with caustic alkali solution require much attention to prevent creeping, and it is impossible to avoid some loss as spray. If the ignition is carried out with dry powdered caustic alkali, creeping still occurs, while there is some doubt whether the whole of the iodine is recovered. This is particularly the case with dried thyroid, as it is very difficult to grind the undiluted material to a fine powder, and, in consequence, it is often found that the apparent iodine-content of the material increases after it has been diluted and ground with lactose.

In order to avoid the errors due to the addition of oxidising substances to the melt, and to loss of iodine by volatilisation, I proposed the ignition of the thyroid with sodium carbonate in a double crucible (*Quart. J. Pharm.*, 1929, 2, 536). In this method the substance is mixed with powdered sodium carbonate in a small crucible which is then filled with the carbonate and inverted on a layer of carbonate in a larger crucible, the space between the two being filled up with the carbonate. The two crucibles are heated in a large and fairly hot flame, so that the carbonate at the bottom and sides of the large crucible is hot before the gases produced by the decomposition of the organic matter pass through it. No attention is required during the ignition, and there is no danger of loss of iodine by creeping or volatilisation. Thorough extraction with hot water, however, is essential, so that after the carbonate has been dissolved in water and the solution filtered, the residue is again boiled with water for half-an-hour.

The Oxidation and Titration.—The oxidation of the iodine to iodate may be carried out by potassium permanganate in alkaline solution (Grützner, *loc. cit.*; Pickworth, *loc. cit.*), the method adopted officially in the German Pharmacopoeia. As, however, the removal of excess of oxidising agent is a comparatively long process, it is generally preferable to use a halogen as oxidising agent.

When a nitrate has been used in the fusion, sodium bisulphite is added in order to prevent the loss of free iodine due to the nitrous acid formed on acidification, and the solution is then either neutralised to methyl orange, or acidified with phosphoric acid. The oxidation of the iodide to iodate is carried out by the addition of chlorine water (Schulek and Stasiak, *loc. cit.*), sodium hypochlorite (Hunter, *loc. cit.*), bromine (Kendall, *loc. cit.*; Kelly and Husband, *loc. cit.*), or bleaching powder solution (Kolthoff, *Z. anal. Chem.*, 1921, 60, 403). Excess of halogen is removed by boiling, and the last traces by the addition of sodium salicylate or phenol. The solution is then titrated, after the addition of potassium iodide, with standard thiosulphate solution.

There is thus no agreement regarding the three essential factors of the determination—the degree of acidity of the solution, the nature of the oxidising agent, and the method for its removal.

The degree of acidity of the solution depends on the method used for the ignition. If nitrate has been used, the product will contain nitrite. On treatment with bromine, nitrate and bromide are formed, and both of these may, under certain conditions, interfere with the determination. In order to avoid this, the acidity of the solution should be kept comparatively low by the use of phosphoric acid for the acidification. When no oxidising substance is added to the melt sulphuric acid may be used for the acidification (Pickworth, *loc. cit.*), and this gives a sharper end-point. The addition of sulphite to prevent loss of free iodine on acidification is unnecessary when no oxidising compounds are present.

Of the halogen oxidising agents mentioned above, chlorine water and solutions of hypochlorites cannot be relied on, as they often contain traces of chlorates, while even bromine water is open to suspicion unless freshly prepared. For a similar reason it is not permissible to add bromine to the alkaline solution before acidification, owing to the risk of producing traces of bromate which, though they may not cause serious error when comparatively large amounts of iodine are to be determined, destroy the accuracy of determination of such small quantities of iodine as are here in question. An advantage incidental to the use of bromine is that the approximate amount present may be judged by the colour of the solution, while it is also more easily removed by boiling than is chlorine.

After boiling, a relatively large amount of bromine may still be present in the solution, although no yellow colour can be detected. Prolonged boiling leads to loss of iodate, and it is, therefore, not advisable to attempt to remove all traces of bromine by boiling, but to use for this purpose a compound which combines with bromine but not with iodine. Salicylic acid has the disadvantage that, unless all but faint traces of bromine have been first removed, the end-point during the final titration with thiosulphate is less definite, owing to a tendency of the blue starch-iodide colour to return. The use of phenol is free from this disadvantage.

For the removal of the halogen it is usual to boil for a considerable time; this leads to loss of iodate, particularly if potassium nitrate has been used in the initial fusion, since the nitrous acid formed on acidification is oxidised by bromine, forming potassium bromide which, on prolonged boiling, reacts with the iodate and causes a reduction in the titre of the solution.

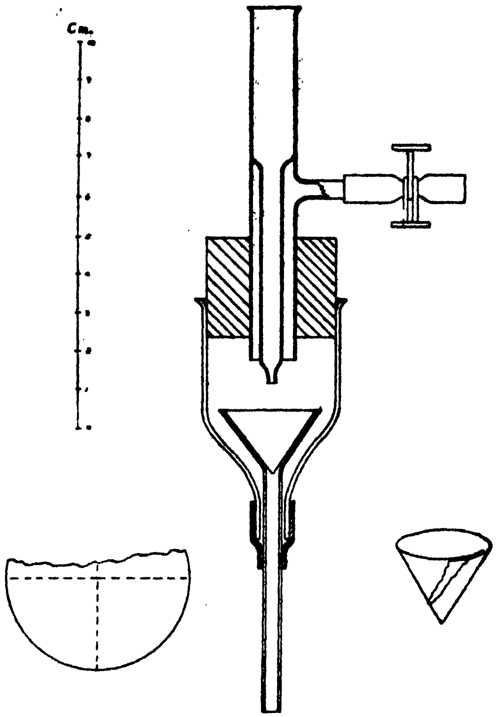
Although the latter source of error is absent when no oxidising agent is used in the fusion, I have found that the best results are obtained if the boiling is stopped while bromine is still just visible in the solution. After cooling, the excess is removed by the addition of phenol, conveniently added as a 25 per cent. solution of crystalline phenol in glacial acetic acid. Provided that at least two minutes are allowed between the addition of the phenol and of the potassium iodide, perfect blanks may be obtained, and there is no danger of low results due to prolonged boiling.

Experiments were also made with sodium cinnamate, maleic acid, or formic acid for the removal of traces of bromine. The objection to the first of these is the sparing solubility of cinnamic acid; maleic acid combines comparatively slowly with bromine; while with formic acid a large excess must be used.

Kendall (*loc. cit.*) has paid considerable attention to the smooth boiling of the solution. Having tried and rejected sand, brick, glass, granite, pumice, capillary tubes, paper fibres, charcoal, porcelain, and coke, he finally used a piece of hard coal, which was removed from the solution before adding potassium iodide. The use of talc and similar powders is undesirable, as the end-point is less distinct in a turbid solution, while porous substances are objectionable because they are liable to retain a little bromine. In a blank determination with 1 grm. of broken pipeclay, I obtained a reading of 0·04 c.c. of $N/100$ thiosulphate solution. The error, therefore, is not negligible if more than 0·1 grm. of this material is used. It may, however, be reduced by pouring off the solution from the pipeclay before adding potassium iodide. In place of adding substances of this nature it is better to facilitate boiling by passing a current of carbon dioxide through the hot liquid.

The details of the method recommended for the determination of total iodine (*vide infra*) have been based on the results of a large number of experiments carried out with definite quantities of standard solutions of potassium iodide and iodate. Proof of the accuracy of the method was obtained by determining the iodine in an acidified solution of sodium carbonate to which had been added 5·0 c.c. of a standard solution of potassium iodide containing 0·4 mgrm. per c.c. The titration results were 7·26, 7·20, 7·14, 7·14, 7·12, 7·14 c.c. of $N/100$ thiosulphate solution, respectively (theory 7·23 c.c.). Blank determinations made without the addition of iodide gave zero readings. To prove that no iodine was lost through its adsorption on the carbon produced in the ignition, 0·1 grm. of thyroxine was dissolved in 0·5 c.c. of N sodium hydroxide solution and made up to 10 c.c. with alcohol. Of this solution, 0·2 c.c. was dried with sodium carbonate and ignited as described. Another portion of 0·2 c.c. was dried with 0·5 grm. of a mixture in equal parts of casein and lactose, and the iodine in the mixture was determined. The titrations in the two cases were 6·15 and 6·18 c.c., respectively. Finally, three determinations were made of the total iodine of a sample of standardised thyroid, the titration readings obtained being 5·18, 5·22, 5·18 c.c. The results obtained by the proposed method are thus shown to be consistent and accurate.

DETERMINATION OF ACID-INSOLUBLE IODINE.—For this purpose Harington and Randall (*Quart. J. Pharm.*, 1929, **2**, 501) employ Kendall's method of determining iodine, and calculate the difference between the total iodine of a solution obtained by boiling the thyroid with alkali and the iodine in the same solution after acidification and filtration. The errors inherent in Kendall's method have been discussed above. It is always undesirable to determine a quantity indirectly, especially when the original figures are subject to error. By igniting with sodium carbonate, as described above, the iodine may be determined directly on the acid-insoluble precipitate, only one experimental error, and that a very small one, being thus involved. In the method described below the essential details of the hydrolysis and the precipitation as given by Harington and Randall (*loc. cit.*), and now adopted in the *British Pharmacopoeia*, 1932, are retained, the precipitate being collected on a filter paper of 45 mm. diameter. To avoid the rather tedious process of continual filling of such a small filter, the apparatus shown in the figure has been devised. The liquid to be filtered is poured into the tube, and drops into the funnel at the same rate as the liquid filtering through, while the side tube and the spring clip allow of the release of air for filling the filter. It is essential that there should be no air-passage between the filter paper and the funnel; this is attained by tearing the paper, after it has been folded into quarters, as shown in the diagram, the wet paper being then fitted closely to the funnel. After the filtration, the filter paper and precipitate are dried at 100° C. The precipitate becomes tarry on heating, some liquid being liberated, and it is therefore necessary to dry the paper and precipitate in the crucible in which they are to be ignited. When dry, the paper with the precipitate is ignited with sodium carbonate.



After the hydrolysis of thyroid with sodium hydroxide Harington and Randall filter the solution. This operation is rather troublesome, as the solution forms a jelly when cold. A determination of the iodine in the alkali-insoluble residue from 10 grms. of standardised thyroid gave a titration reading of 1·0 c.c. of $N/200$ thiosulphate solution, equivalent to 0·05 c.c. of $N/100$ thiosulphate solution on 1 grm. of material. Thus filtration of the alkaline solution does not appear necessary.

In order to check the method 10 grms. of thyroid were heated beneath a reflux condenser for 4 hours with 100 c.c. of N sodium hydroxide solution, the product was filtered as quickly as possible through a hot sintered-glass crucible, and the filtrate and washings were made up to 500 c.c. Fifty-c.c. portions of this solution were treated with acid, and the acid-insoluble iodine was determined as described below. The titration readings were 4·31, 4·30 c.c. of $N/100$ thiosulphate and 8·70 c.c. of $N/200$ thiosulphate solutions, respectively.

Details of Procedure.—*Total Iodine.*—The dried thyroid (0·5 grm.) is weighed into a nickel crucible of 26 mm. diameter and mixed with about 1 grm. of pure dry powdered sodium carbonate. The crucible is filled with the carbonate and inverted on a layer of sodium carbonate at the bottom of a large crucible of 36 mm. diameter, and more sodium carbonate is added to fill the space between the two crucibles. The two crucibles are then heated for twenty minutes so as to raise the outside of the larger crucible to a dull red heat. When cold, the contents of the larger crucible are tipped into about 100 c.c. of water and broken up immediately to avoid caking, and the larger crucible is rinsed out. After being boiled for 10 minutes the solution is filtered into a 600-c.c. conical flask through a hardened filter paper, or through a sintered-glass filter (1 G4 or 3 G4), and washed. The residue on the filter paper is washed back into the beaker by means of a jet of water, and the extraction is completed by boiling with another 100 c.c. of water for thirty minutes. The filtrate and washings are cooled, made up to about 400 c.c., and, after the addition of methyl orange, 50 per cent. sulphuric acid is introduced until the mixture is just acid. After the addition of 10 c.c. of 10 per cent. sulphuric acid in excess and a few drops of iodine-free bromine, the solution is heated; and when it begins to boil a current of carbon dioxide is passed into it to prevent bumping. The heating is stopped when the solution has only a slight yellow colour (after about 3 minutes' boiling), and the solution is cooled. About 0·2 c.c. of a 25 per cent. solution of crystalline phenol in glacial acetic acid is then added, and, *after the lapse of at least two minutes*, a few crystals of potassium iodide are added, and the mixture is titrated with $N/100$ thiosulphate solution, with starch as indicator.

Acid-insoluble Iodine.—One grm. of the thyroid is boiled for four hours beneath a reflux condenser with 10 c.c. of N sodium hydroxide solution. The solution is diluted to about 25 c.c., filtered as hot as possible through a previously-warmed sintered-glass filter, and the residue is washed with a little hot water. The filtrate is transferred to a beaker and acidified with 11 c.c. of N sulphuric acid; the reaction of the mixture is then adjusted, if necessary, to be slightly acid to congo red paper. After standing overnight the clear liquid is decanted, and the precipitate is collected on a 45 mm. filter paper (preferably with the aid of the filtration device shown in the diagram) and washed with water. The filter paper (with the precipitate) is transferred to a nickel crucible of 26 mm. diameter and dried. A little powdered sodium carbonate is then placed at the bottom of the crucible and in the filter, and the latter is completely embedded in the carbonate. The subsequent ignition in a double-crucible, extraction and treatment of the solution are exactly as described for the determination of the total iodine in the material.

STANDARDISATION OF THYROID.—The standardisation of thyroid on a basis of acid-insoluble iodine-content, determined by the method described, requires only one determination of iodine. It is neither practicable nor necessary to fix a second standard for total iodine-content. The determination of "inorganic" iodine (*i.e.* iodine compounds soluble in cold water) in order to detect adulteration by the addition of iodides no longer serves any useful purpose.

NOTE.—In a recent paper by Leland and Foster (*J. Biol. Chem.*, 1932, 105) there is described a method of determining thyroxine by shaking out into butyl alcohol after alkaline hydrolysis. These authors consider that the results obtained by the method of Harington and Randall are too high. Further investigation of the separation of thyroxine from thyroid is necessary before the problem of the chemical assay of thyroid can be considered fully solved. This investigation must be based on the iodine-content of different fractions; for this, the first requirement is an accurate and reliable method of determining the iodine in them. The methods described in this paper may, therefore, prove helpful in the final solution of the problem, even though the "acid-insoluble iodine" process may be found not to effect a sufficiently complete separation of thyroxine.

I wish to record my thanks to the Directors of The British Drug Houses, Ltd., for permission to publish this paper.

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The Iodine and Thiocyanogen Values of Irish Butter

By PAUL ARUP, Ph.D., F.I.C.

(*Read at the Meeting, May* 4, 1932)

The results recorded in this paper are taken from a series of observations made in connection with the investigation of the consistency of Irish butter—a property which depends, among other factors, on the content of unsaturated glycerides. Since the method devised by H. P. Kaufmann (Analyst, 1926, **51**, 157, 264) for determining linolic, as well as oleic glycerides, in oils appeared to offer possibilities as a routine method for the examination of large numbers of samples, it was decided to attempt to apply it to butter fat, for the data hitherto obtainable by other and more elaborate methods have of necessity been comparatively few. It may be noted that in the present account, the terms "oleic" and "linolic glycerides" are only intended to indicate the combined acids in the glycerides, without reference to the mixed or simple character of the glycerides.

Iodine Value.—The unsaturated constituents of butter fat, of which this value gives a total measure, have been shown by Hilditch and Jones (Analyst, 1929, **54**, 85), and by Hilditch and Sleightholme (*Biochem. J.*, 1930, **24**, 1096; 1931, **25**, 507) to consist essentially of oleic and linolic glycerides. The main object of the present investigation was to study broadly the seasonal variations of these constituents in Irish butter. Some foreign butters were analysed for comparison.

The seasonal variations in the iodine value of Danish butter have been studied by Kilde and Winther (*Milchwirtschaftl. Forsch.*, Bd. **10**, Heft 3, 228), who found that the figures for mixed average samples varied from 29·9 in December, 1928, to 41·4 in August, 1929. Similarly, Haglund, Wode and Olsson (*Bull.* 387 [1930], *Centralanstalten*) found the average iodine values of Swedish butter to vary from 31·0 in January and February to 40·0 in August and September. The fall in iodine value during winter in these countries is regarded as undesirable, as it renders the butter too firm; this matter received some attention at the International Dairy Congress, held in Copenhagen in 1931, at which the following resolution was passed:—"In view of the importance for the production and the consistence of winter butter, of the amount of fat contained in oil-cakes and of their composition, the Congress recommends that the manufacturers of, and dealers in, oil-cakes should consider the possibility of bringing an oil-cake on the market which would be guaranteed to contain at least 5 to 6 per cent. of oil, and, if the oil-cakes are sold in mixture, of a mixture containing sunflower-seed cakes and rape cakes in at least the same quantity as coconut or palm-kernel cakes or soya meal." This resolution was largely the result of an extensive series of feeding experiments which were carried out under practical conditions during the three winter seasons, 1927–30, at the Danish State Experimental Dairy by A. P.

Hansen; an account thereof was published by the Congress as Paper No. 85, Section 3.

The seasonal variations in the iodine value of Danish butter are considered to be due wholly to the winter-feeding factor; there is no lactation factor to be considered, as is very probably the case with Irish butter. From the results now to be discussed, it will be seen that the iodine value of Irish butter is also affected by a winter-feeding factor, though to a modified extent; in this account the term "winter-feeding factor" is intended to include such concomitant factors as the influence of the change from outdoor to indoor life and seasonal variations in temperature, but not the influence due to the stage of lactation.

Table I shows the results obtained from iodine-value determinations carried out on mixed average samples each month; during the greater part of the year, the number of individual samples represented by each mixed average sample was about 400; the number decreased to a minimum of 50 in December.

TABLE I

MIXED AVERAGE SAMPLES OF BUTTER FAT

	Month	Iodine value (Wijs)	Reichert–Meissl value	Polenske value
1931	May	38·7	31·4	2·80
	June	39·3	30·8	2·75
	July	40·0	30·4	2·30
	August ..	41·0	28·6	2·15
	September ..	41·3	27·6	2·10
	October ..	43·0	26·5	1·90
	November ..	42·3	25·6	1·80
	December ..	41·3	24·7	1·75
1932	January ..	39·6	27·0	1·95
	February ..	39·5	27·7	1·95
	March	38·3	29·9	1·95
	April	38·3	30·0	1·90
	May	38·2	31·1	2·30
	June	38·1	31·9	2·85
	July	39·2	31·8	2·50
	August ..	41·4	30·4	2·10

In the case of Irish winter butter there are probably two factors—the winter-feeding factor, which tends to lower the iodine value, and the lactation factor, the effect of which is to raise the iodine value at times when the Reichert–Meissl value is decreasing, and conversely. The seasonal changes in the latter and in the Polenske value are generally recognised as lactation phenomena, and it is reasonable to suppose that the corresponding movements in the iodine value in the opposite sense, which occur regularly during the greater part of the year, are assignable under the same heading. It will be seen that in 1932 the minimum iodine value and the maximum Reichert and Polenske values occurred later than in 1931. This is attributable to the fact that the butter-making season was a late one in 1932.

The influence of the winter-feeding factor becomes evident in November, *i.e.* two months later than in the case of the Danish and Swedish butters; this difference is, no doubt, due largely to climatic factors, and may also be partly due to the counteracting influence of the lactation factor which would tend to retard the fall in the iodine value during the latter half of the year. The fact that the extent of the variation between summer and winter iodine values is only about one-half of that experienced in the other countries mentioned may well be explained by the supposition that the two factors tend to counteract one another, especially during the spring and autumn months. Further, the difference between summer and winter feeding is not so pronounced in Ireland as in some other countries.

THIOCYANOGEN VALUE.—Kaufmann (*loc. cit.*) has shown that linolic acid or glyceride combines with thiocyanogen only at one of the two double bonds, so that a knowledge of the thiocyanogen absorption (generally calculated in terms of iodine) and of the iodine value makes possible the calculation of the linolic and the oleic glyceride content of a fat. For the preparation of the thiocyanogen solution, the method recommended by Kaufmann (ANALYST, 1928, **53**, 613) was used; the solvent was pure glacial acetic acid (99–100 per cent.) containing 10 per cent. of acetic anhydride, and the mixture was kept at least a week before use. Twenty-five grms. of carefully dried, pure lead thiocyanate were added to 500 ml. of the solvent, and 3 ml. of bromine to another 500 ml. The latter solution was added to the former, and the mixture was shaken until colourless, allowed to settle, and then filtered through a dry filter paper. On titration, Kaufmann has shown that this solution must be poured into an excess of potassium iodide solution, when iodine will be quantitatively displaced by thiocyanogen, and may be titrated by means of thiosulphate as usual. If the potassium iodide solution is poured into the thiocyanogen solution, a little loss of thiocyanogen by hydrolysis takes place. The solution, prepared as described, is approximately decinormal in strength; it should be kept in the dark and protected from access of moisture; its stability depends, to some extent, on the purity of the materials used in its preparation; during the first 3 or 4 days a loss in strength corresponding with not more than about 0·5 to 0·1 ml. per 25 ml. per day may usually be expected; for reasons stated below it is advisable to use the solution as fresh as possible.

The general outline of the determination of the thiocyanogen value is similar to that of the iodine value method according to Wijs. It would appear that the work hitherto carried out has been on oils or fatty acids which remain in solution in the acetic acid solvent; most solid fats, including butter fat, however, partly crystallise out of solution in 2 to 3 hours at 22° C., even when the 25 c.c. of thiocyanogen solution is diluted with twice its volume of the acetic acid and anhydride mixture, the amount of fat taken being 0·25 to 0·30 grm.

Some trials were made with carefully purified and dried carbon tetrachloride and petroleum spirit (ligroin) as fat solvents, as in iodine-value determinations, but it was found that the absorption of thiocyanogen was inhibited to a considerable extent in such cases; it was therefore decided to raise the temperature at which the absorption mixture was kept at 25 to 26° C. In order to study what effect this raising of the temperature might have on the accuracy of the results, some comparative trials were made at two temperatures, *viz.* 16 to 18° C. and 25 to 26° C., with olive and arachis oils. For the lower temperature, 0·2 grm. of the oil was dissolved in 25 ml. of the thiocyanogen solution, and for the higher temperature, the same weight of oil was first dissolved in 25 ml. of the acetic acid and anhydride mixture, after which 25 ml. of the thiocyanogen solution were added; the absorption mixtures were contained in well-stoppered 100-ml. bottles and kept at the respective temperatures together with blanks. The results were as follows:

Oil		Absorption time Hours	Thiocyanogen value (16 to 18° C.)	Thiocyanogen value (25 to 26° C.)
Olive	..	4	76·0	75·8
,,	..	5	75·9	75·6
Arachis	..	16	69·7	69·3

It will be seen that there is a tendency for somewhat lower thiocyanogen values to be obtained at the higher temperature than at the ordinary temperatures, and that this is accentuated with longer absorption periods. The latter point (*i.e.* the effect of the absorption time) can be verified from Kaufmann's results. As the thiocyanogen solution is not quite stable even when freshly made, there will always be a tendency for more loss of free thiocyanogen to occur by polymerisation in the blank tests than in the actual absorption tests; this will cause the blank values to be slightly low, and thus decrease the apparent absorption. At higher temperatures the rate of deterioration of the thiocyanogen solution is somewhat increased; thus in the olive oil experiments the blank values were 26·25 ml. and 26·1 ml., when working at the lower and the higher temperatures, respectively.

It thus follows that the error inherent in the method due to the deterioration of the thiocyanogen solution is increased with longer absorption periods and higher absorption temperatures. In the case of the more highly unsaturated oils, periods of twice to three times that necessary for butter fat are required; it may, therefore, be presumed that the results obtained for butter fat, in spite of the temperature error, will be comparable with those obtained for the oils as regards reliability. From what has been said, it will be understood that the linolic glyceride percentages given below in Table II may be somewhat high, possibly from one-third to one-half of a unit per cent., but they may, at any rate, be used for comparative purposes, such as in the study of seasonal variations.

METHOD OF DETERMINING THE THIOCYANOGEN VALUE OF BUTTER FAT.—Quantities of 0·25 to 0·30 grm. of the fat were weighed out in small tubes, which were introduced into 150-ml. conical flasks furnished with well-fitting glass stoppers. The flasks were gently warmed, just sufficiently to melt the fat, whereupon 25 ml. of the acetic acid and anhydride mixture at 38° C. were added, followed by 25 ml. of the thiocyanogen solution after the fat had been dissolved. The absorption flasks, with blanks, were placed in an incubator at 25 to 26° C. for 7 hours, this having been determined as the minimum time required for the maximum absorption by butter fat. For titration, the contents of the flasks were poured into 40 ml. of 5 per cent. potassium iodide solution, and the liberated iodine was titrated with $N/10$ thiosulphate and starch in the usual way; towards the end of the titration, some of the solution was used to rinse out the remains from the absorption flask, and the titration was continued to the end.

The thiocyanogen values were expressed in terms of iodine absorbed, and the percentages of combined linolic and oleic acids were calculated. The difference between the iodine and thiocyanogen values, divided by the factor 0·905, gives the percentage of linolic acid.

The results of the determinations are given in Table II. The samples include Irish summer and winter butters and some foreign butters.

TABLE II

IODINE AND THIOCYANOGEN VALUES OF BUTTER

Date	Description	Iodine value	Thiocyanogen value	Linolic acid Per Cent.	Reichert–Meissl value	Polenske value	Mark creamery
Dec. 1930	Irish creamery	42·4	38·7	4·1	21·1	1·65	A
		43·0	39·6	3·8	22·7	1·55	B
		42·0	39·0	3·3	21·5	1·50	C
		43·2	40·0	3·5	22·2	1·60	D
		41·8	38·7	3·4	20·7	1·40	E
		42·1	38·2	4·3	21·8	1·40	F
		42·5	38·8	4·1	21·1	1·55	G
		43·0	39·2	4·2	22·2	1·35	H
		43·0	39·2	4·2	22·1	1·50	I
		42·6	38·8	4·2	22·2	1·50	J
	Average	42·56	39·02	3·91			
June 1930	Irish creamery	37·0	34·0	3·3	31·5	2·80	A
		38·3	34·2	4·5	31·3	3·15	B
		38·1	34·7	3·8	30·7	2·40	C
		37·1	33·6	3·9	32·2	3·25	D
		37·3	33·5	4·2	31·1	3·10	E
		37·1	32·9	4·6	30·9	3·10	F
		38·7	35·7	3·3	31·2	3·05	G
		37·5	34·5	3·3	31·6	2·75	H
		39·0	34·8	4·6	30·0	2·80	I
		38·0	33·8	4·6	32·1	2·90	J
		36·8	33·4	3·8	31·5	2·80	K
	Average	37·72	34·10	3·99			
Feb. 1931	New Zealand	32·6	28·8	4·0			
	Danish	31·9	28·0	4·3			
	,,	32·5	29·5	3·3			
	,,	30·6	27·6	3·3			
June 1931	Australian	34·5	31·2	3·6			
	Siberian	33·8	30·6	3·5			
	Argentine	39·4	35·7	4·1			

The variations in the combined linolic acid were from 3·3 to 4·3 per cent. for the Irish winter butter samples, from 3·3 to 4·6 for the Irish summer butters, and from 3·3 to 4·3 for the seven foreign butters.

Table III has been drawn up to show the composition of the unsaturated acids (assuming these to consist of oleic and linolic acids only) in the various classes of butter; where these were represented by more than one sample, the results were averaged.

TABLE III

Description of butter		Oleic acid in fat Per Cent.	Linolic acid in fat Per Cent.	Linolic acid in unsaturated acids Per Cent.	Number of samples represented
Irish winter	..	39·02	3·91	9·1	10
Argentine	..	35·2	4·1	10·4	1
Irish summer	..	33·54	3·99	10·6	11
Australian	..	30·8	3·6	10·5	1
Siberian	..	30·3	3·5	10·4	1
Danish	..	27·61	3·63	11·6	3
New Zealand	..	27·5	4·2	13·2	1

From the first column of figures it is seen that the results have been entered in order of descending percentages of oleic acid (obtainable from the fat); the third column of figures shows that there is a definite tendency for the percentage of linolic acid in the total unsaturated acids to increase as the percentage of oleic acid in the fat decreases. There is thus a tendency for the linolic glyceride-content to remain approximately constant, whilst the oleic glyceride-content is the variable factor. It is noteworthy that these relationships should be found between samples differing so widely in origin as those which have been examined.

In conclusion, I wish to express my thanks to the Department of Agriculture, Dublin, for permission to publish this paper.

BUTTER TESTING STATION,
HARCOURT TERRACE, DUBLIN

Tests for the Keeping Quality of Unsalted Butter

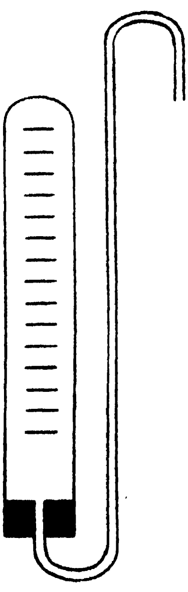
BY J. T. MINSTER, B.SC., A.I.C.

IT is a well-known fact that unsalted butter which has been kept for a month or two in cold store, *e.g.* during transport from the Dominions, very frequently deteriorates rapidly in flavour when it is again exposed to normal atmospheric conditions.

Possible causes of this deterioration are direct oxidation due to contact with the air, and the action of micro-organisms. The oxygen absorption was followed by a development of Issoglio's "oxidisability" method,[1] and it was found that this property cannot be correlated with the specific complaint under consideration, although it may have a bearing on changes which occur later when the butter is quite rancid. The tests here described are concerned essentially with the first stages in deterioration. The work on the oxygen absorption involved keeping the samples at 37 to 38° C. for several days, and it was observed that some tended to putrefy, whilst others remained sweet, indicating that bacteriological development was proceeding along different lines in the various samples. The following tests for enzymes and micro-organisms were employed:

(1) THE CATALASE TEST.—True lactic acid bacteria do not give rise to the enzyme catalase, whereas putrefactive organisms very frequently do so. Other bacteria which are objectionable from the butter-making point of view, and many of which occur in dirty water, also develop catalase. Therefore, if a butter is found to be rich in catalase, it may be deduced that the conditions of its manufacture were imperfect, and that objectionable organisms have gained access to it.

The technique employed—practically that of Orla-Jensen,[2] with the use of Ling's apparatus, as modified for butter-testing by Hesse[3]—is as follows:—Weigh 100 grms. of butter into a wide-mouthed separating funnel with a stem about 1 cm. long. Close the end of the stem with a small rubber stopper, and stand the funnel in a water bath at 45° C. until the butter is melted. Add 40 c.c. of distilled water at 45° C., and mix thoroughly. When separation has taken place, run off the aqueous layer, and place 15 c.c. of this in a graduated test-tube of 20 c.c. total capacity. Add about 3·5 c.c. of hydrogen peroxide (10 vol.), and mix by inverting the tube three times. Fill the tube completely with hydrogen peroxide and insert the rubber stopper and delivery tube as shown in the figure. Keep in a water-bath at 37 to 38° C. for six hours. Read the volume of gas evolved, shaking to disperse foam, if necessary.



The results become more expressive when arranged in an arbitrary scale in which the result 0 c.c. has a value of 100. Very rarely is 8 c.c. exceeded, and this volume (or more) is taken as zero. As a matter of experience, it was found that the difference in quality between a sample giving, say, 4 c.c., and one giving 6 c.c., is very slight, whereas the difference in quality between 0·1 c.c. and 2·1 c.c. is very great. The important section is from 0 to 2 c.c., and the scale has, therefore, been arranged as a curve giving a drop of 100 to 50 for 0 to 2 c.c., and 50 to 0 for 2 to 8 c.c. The equation employed is $C = 100 - 35{\cdot}35\sqrt{V}$ where V c.c. represent the volume of gas, and C the catalase value.

(2) REDUCTASE TEST.—The time taken for milk coloured with methylene blue to become decolorised under standard conditions is a function of the number and type of organisms present, and affords a fair criterion of cleanliness and keeping quality (*cf.* ANALYST, 1926, **51**, 459; 1928, **53**, 106, 213, 532). It may be applied to the examination of butter in the following way:—Place 10 c.c. of the aqueous extract, as prepared for the catalase test in a test-tube, 0·5 inch in diameter. Add 0·5 c.c. of a 0·005 per cent. solution of methylene blue. Mix by inverting the tube with as little dispersal of air as possible. After a few minutes, to allow air bubbles to escape, pour a layer of melted petroleum jelly on to the surface. Place the tube in the water-bath at 37 to 38° C., and note the time taken to bleach the dyestuff.

An arbitrary system of recording results has again been adopted:

Bleached in 0·5 hour or less	0
If any blue is present after 6 hours, but none after 21 hours	90
,, ,, ,, 21 ,, ,, ,, 24 ,,	95
,, ,, ,, 24 hours	100

Between the points 0·5 hour = 0 and 6 hours = 90 the results lie on the straight line $R = 16{\cdot}36t - 8{\cdot}18$, where t hours = time required for decolorisation, and R = reductase value.

In order to obtain additional information regarding the organisms present in the butter, without going to the extent of plate counts, the following tests have been employed.

(3) CULTURE MEDIA TUBES.—Prepare the following culture media:

(*a*) *Litmus Milk.*—Skim milk, 1 litre; azolitmin, 1 grm.

(*b*) *Purple Salt Agar.*—Beef extract, 3; peptone, 5; agar-agar, 15; sodium chloride, 8; bromcresol purple, 0·025 grms., per litre. (Adjust p_H to 7·4.)

(*c*) *Purple Lactose Agar.*—Beef extract, 3; peptone, 5; agar agar, 10; lactose, 10; bromcresol purple, 0·025 grms., per litre. (Adjust p_H to 6·8.)

Place 10 c.c. of each medium in test-tubes, and plug and sterilise them in the usual way. Melt the contents of the tubes in boiling water and afterwards cool them to as low a temperature as possible consistent with the media remaining fluid. By means of a clean dry pipette place 1 c.c. of the aqueous butter extract in each of the three tubes. Mix well and cool, allowing the agar to harden to form a slant. Incubate at 37 to 38° C. for 16 hours.* At the end of this period award points according to the condition of the tubes, in accordance with the following scale:

(*a*) *Litmus Milk.*

Colour	Bleached	0	Curd	Bad curd (torn and liquefied)	0
	Part bleached (but at least 50 per cent. remaining unbleached)	1		Moderate curd (few holes and channels and little liquid in a mostly solid curd)	1
	Entirely unbleached	2		Good curd (uniformly solidified, or not even solidified)	2

Maximum for litmus milk, 4.

Note.—For types of curd see Orla-Jensen, *Dairy Bacteriology*, 1921, p. 164.

(*b*) *Purple Salt Agar.*

Colour below the slant	Yellow	0	Gas	Blown and distended with gas		Surface growth	Heavy	0
	Yellow-purple	1		Isolated individual bubbles	1		Moderate	1
	Purple	2		No gas	2		Trace or nil	2

Maximum for purple salt agar, 6.

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* This test may be made more exact by observing the usual precautions to ensure sterility throughout the experiment.

Notes.—Colour : Organisms which form acid in the absence of lactose are particularly undesirable, as this indicates some action on the proteins akin to putrefaction.

Gas : Gas-forming organisms in butter indicate lack of cleanliness at some stage of the manufacture.

Surface growth : This may be regarded as heavy if more of the surface is covered with growth than is left clear: moderate, if there are more than two or three colonies, but the surface is at least half-free; and as a trace when there are only one or two isolated colonies.

(*c*) *Purple lactose agar.*

Colour below the slant	Yellow. If purple salt agar is purple	1
	″ ″ ″ ″ ″ ″ yellow-purple ..	½
	″ ″ ″ ″ ″ ″ yellow	0
	Purple	0
	Yellow-purple	1

Gas and surface growth as for purple salt agar.

Maximum for purple lactose agar, 5.

Note.—Colour : The presence of a few genuine lactic acid bacteria is regarded as beneficial, tending to keep down the growth of other (more objectionable) organisms. If purple salt agar has given the result "purple," it indicates that any acid-formers are of the true lactic acid bacteria type, and in these circumstances "yellow" in the purple lactose agar test counts higher than if some, at least, of the acidity is due to organisms acting on the proteins.

Add the totals for the three different tubes, multiply by 100/15 and regard the result as a percentage.

(4) THE INCUBATION TEST.—Incubation at 37 to 38° C. for four days has been employed as follows:—Fill a glass-stoppered jar from half to three-quarters full with the sample. Melt in a water-bath at 45° C., and shake well. Incubate for four days at 37 to 38° C. Shake daily, and observe the odour immediately *before* shaking each day.

The results of this test depend very largely on the judgment and experience of the observer, and, for this reason and others stated later, great reliance is not placed on it. Removing the jar of butter from the incubator and allowing it to cool increases the intensity of any unpleasant smell. This might be advantageous as a regular practice, but all the results given in this paper have been obtained by examining the samples while warm.

The following marking system has been adopted:

Very pleasant warm, sweet, butter-smell	100
Odourless	85
Slightly stale, musty or sour, but with no trace of putrefaction ..	70
Distinctly stale, musty or sour, or very faintly putrid	50
Distinctly putrid and unpleasant	30
Extremely offensive	0

The average of the figures for the four days is taken as the result of this test.

For the final evaluation of the butter the average of the four results—catalase, reductase, culture media tubes and incubation is taken, and, in general, the results are in agreement, a low catalase figure accompanying a low reductase figure, etc. This is not invariably the case, however, and the average figure has been found more trustworthy than any of the individual results. If one value is much below the average the butter frequently has some unusual characteristic. For example, butter number 13 (for which figures are given below) had a very rank flavour when sampled, but this became no worse on keeping for some weeks.

The table below shows typical figures for butter samples giving high and low results. A figure of 70 or more is taken as indicating good keeping quality.

TABLE I

Sample	No.	Catalase	Reductase	Culture media tubes	Incubation	Average
Good	1	100	100	100	65	91
,,	2	100	95	84	85	91
,,	3	100	100	71	80	88
,,	4	95	90	63	80	82
,,	5	85	86	63	76	77
,,	6	78	68	87	65	74
Poor	7	75	50	73	60	65
,,	8	53	40	63	60	54
,,	9	42	24	33	75	43
,,	10	34	50	41	40	41
,,	11	39	28	27	55	37
,,	12	17	30	25	50	31
Erratic-poor	13	19	90	100	44	63
,,	14	0	5	21	80	27

RESULTS IN PRACTICE.—Practical proof of the applicability of these results to the problem of keeping butter under ordinary domestic conditions has been obtained.

(1) Two samples of butter, one with high and the other with low figures, were packed in 1-lb. blocks, wrapped in vegetable parchment, and kept at room-temperature for four days. On inspection, the sample with the higher value was found to be still fresh and sweet, whereas that with the lower values had a very obvious stale smell and taste. The same determinations as before were then carried out.

TABLE II

		Catalase	Reductase	Culture media tubes	Incubation	Average
High	Original	95	100	53	80	82
	After 4 days	90	100	52	80	81
Low	Original	66	60	20	75	55
	After 4 days	13	5	5	75	25

The high values changed hardly at all during this period, but the low original values dropped considerably, with the exception of those given by the incubation test, which gave no indication of the difference in quality either between the two samples in their original or final state, or between the low-valued sample before and after the 4 days' storage.

In a similar experiment with entirely different samples, the following results were obtained:

TABLE III

		Catalase	Reductase	Culture media tubes	Incubation	Average
High	Original	87	88	57	55	72
	After 7 days	75	80	50	45	63
Low	Original	53	16	40	45	39
	After 7 days	12	11	37	45	26

The sample with lower values gradually deteriorated until, after two weeks, it was too unpalatable to use. The one with higher values was still in good condition, and remained so until some time afterwards.

(2) The tests were applied to several samples which had been kept until they showed the objectionable characteristics which this work was carried out to investigate. The following results, obtained with three of these, are typical:

TABLE IV

	Catalase	Reductase	Culture media tubes	Incubation	Average
1	0	0	20	75	24
2	3	9	20	73	26
3	21	10	9	80	30

The following points arise from the examination of the figures in Tables II, III and IV:

(*a*) Low catalase, reductase and culture media tube figures are characteristic of butter which has gone "off," and these low values develop most rapidly in butter which has original sub-normal values.

(*b*) It is questionable whether the incubation figure has much significance. Samples occasionally occur, however, which give very low results when tested in this way, all the other figures being normal.

TABLE V

	Catalase	Reductase	Culture media tubes	Incubation	Average
1	85	85	—	0	57
2	69	73	65	0	52
3	80	100	65	35	70
4	90	100	55	40	71
5	95	90	81	47	78
6	90	100	91	43	81

A sample which soon gives rise to an extremely objectionable odour at 38° C. must be expected to deteriorate more rapidly under ordinary atmospheric conditions than butter which remains perfectly sweet at the higher temperature.

(3) Many observers all over the country have regularly received samples of butter which have been tested by the methods described above. The samples have been kept under the most varied conditions, including all those met with under

ordinary domestic circumstances. Weekly reports have been received regarding the behaviour of the butter, as judged by the various observers, and the number of unfavourable reports regarding the keeping of the samples has been plotted, together with the results of the tests for keeping qualities. (Atmospheric temperature variations may be excluded; the average temperature was slightly higher when few adverse reports were made, and lower when the number of such reports increased.)

It is not suggested that either the actual determinations, or the methods of expressing the results have a very high standard of precision, and their interpretation must be made in a broad way. Distinction cannot be made between samples because of a difference of a few points, but the figures should be taken more as an indication of the class of butter to which the sample belongs.

SUMMARY.—(1) The onset of the first stages of deterioration of unsalted butter, when exposed to normal atmospheric conditions after a month or two in cold store, could not be correlated with the oxygen absorption.

(2) Methods of estimating the activity of the enzymes, catalase and reductase, are described, together with a simple method for the bacteriological examination of butter, with arbitrary scales for expressing the results.

(3) Incubation for four days at 37 to 38° C. and observation of the odour daily has been employed as a test, and a system of marking is described. Less reliance is placed on this test than on those summarised under (2).

(4) The average of the catalase, reductase, bacteriological and incubation tests has been found to be the most reliable guide to the keeping quality of a butter sample.

(5) Typical results for good and poor samples and for those already in process of deterioration are given. Low catalase, reductase and bacteriological test values are characteristic of butter which has gone "off," and these low values develop most rapidly in samples with original sub-normal values.

(6) The opinion of independent observers on the quality of the butter became more adverse with diminution in the average keeping-quality value.

I wish to thank the Directors of the Dominion Dairy Company, in whose laboratory this work was carried out, for their help and advice and for permission to publish this paper.

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DOMINION DAIRY CO., LTD.,
AYLESBURY, BUCKS.

The Separation and Determination of Traces of Lead in the Presence of Small Quantities of Iron

By J. HUBERT HAMENCE, M.Sc., A.I.C.

In the course of the examination of chemicals (particularly alkali and alkaline earth salts), dyes and foodstuffs, for objectionable impurities, it is often necessary to determine traces of lead which may range between one part and 300 parts per million of the solid under examination. For this purpose the colorimetric method, based upon the formation of a colloidal solution of black lead sulphide in an alkaline medium, is almost invariably employed.

The presence of traces of iron, however, introduces difficulties. Some provision is made for this by preliminary treatment of the solution with potassium cyanide (Teed, Analyst, 1892, **17**, 141; Hill, *Chem. and Drugg.*, 1905, **77**, 388) and Wilkie (*J. Soc. Chem. Ind.*, 1909, **28**, 636) recommended treatment of the solution with sodium thiosulphate prior to the addition of potassium cyanide.

It has been found, however, that when the iron in solution exceeds a few mgrms. it is difficult to prevent (*a*) the precipitation of the iron as hydroxide or sulphide, or (*b*) the formation of a yellow solution which renders the assessment of the lead sulphide difficult.

Adsorption of Lead by Ferric Hydroxide.—The removal of the iron by precipitation as ferric hydroxide leads to very low results, owing to adsorption of the lead on the ferric hydroxide (Wilkie, *loc. cit.*). Three mgrms. of ferric hydroxide will adsorb 1 mgrm. of lead, and this lead is not liberated by re-precipitation of the ferric hydroxide.

By precipitating the iron in the presence of ammonium acetate and boiling the solution until it is just acid the adsorption error is largely reduced, but is not entirely avoided. Thus 3·3 mgrms. of ferric hydroxide were precipitated in a solution containing 2 grms. of ammonium acetate and 5·0 mgrms. of lead, and the liquid was boiled until acid. After being filtered off and washed well with hot water the adsorbed lead was determined by dissolving the ferric hydroxide in nitric acid and separating the lead by the thiocyanate method subsequently to be described; 0·20 mgrm. was found to be adsorbed. Similarly, with smaller amounts of lead, a small percentage always remained adsorbed on the ferric hydroxide.

The large adsorption produced by precipitating the ferric hydroxide in the presence of ammonium acetate and leaving the solution ammoniacal is not always fully realised. The following results were obtained by precipitating 3·3 mgrms. of ferric hydroxide in the presence of ammonium acetate and lead nitrate; after precipitation the solution was heated to 80° to 90° C. in a water-bath for 20 minutes, and the lead was determined in the supernatant solution, which was still strongly ammoniacal.

Ammonium acetate in solution Grms.	Lead added Mgrm.	Lead adsorbed Mgrm.
0·5	1·00	0·96
5·0	1·00	0·72

Even in the presence of 5 grms. of ammonium acetate the adsorption is very considerable.

Errors due to the adsorption by filter paper when ammoniacal solutions of lead are filtered are also considerable and must be avoided.

The existing methods for the separation of lead and iron which are free from adsorption errors are all tedious, with the exception of the method recently described (Allport and Skrimshire, ANALYST, 1932, 440). Their method is based upon the extraction of the lead from an ammoniacal solution with a solution of diphenylthiocarbazone in chloroform, the lead diphenylthiocarbazone complex dissolving in the chloroform. The chloroform solution is subsequently evaporated, the organic matter is destroyed, and the lead in the residue is determined colorimetrically. This excellent method, which can be employed in the presence of many interfering substances, has been found to give good results, but it was thought desirable to find a method for the separation of a mixture of lead and iron which was even more rapid than that of Allport and Skrimshire.

SEPARATION AS THIOCYANATES.—The present method of separation depends upon the properties of lead and ferric thiocyanates. Lead thiocyanate was prepared by the double decomposition of equivalent amounts of ammonium thiocyanate and lead nitrate in aqueous solution. After repeated recrystallisations from hot water, washing with alcohol and ether, and drying at 100° C., a white crystalline product containing 64·05 per cent. of lead was obtained [theory for $Pb(SCN)_2$ = 64·09 per cent.]. This compound contained no water of crystallisation or moisture and gave not the slightest reactions for ammonia or nitrate. It was thus identical with the product obtained by Hall (*J. Amer. Chem. Soc.*, 1902, **24**, 570).

The solubility of lead thiocyanate in water at 12° C. was found to be 3·180 grms. per litre, and at 12° C. it was nearly zero in a mixture of equal volumes of ether and amyl alcohol. Ferric thiocyanate, however, is very soluble in this mixture, and may be extracted from aqueous solution by this solvent. This mixture of ether and amyl alcohol was found to be a far more efficient solvent for ferric thiocyanate than either ether or amyl acetate, in both of which it is soluble.

Since no precipitations are involved in this separation adsorption errors are no longer introduced.

PROCEDURE FOR ALKALI AND ALKALINE EARTH SALTS.—Five grms. of the salt are dissolved in 30 c.c. of water in a separating funnel. To this solution 5 c.c. of 10 per cent. nitric acid and 5 c.c. of saturated ammonium thiocyanate solution are added. The solutions are mixed, 15 c.c. of amyl alcohol and 15 c.c. of ether are added, and the whole is vigorously shaken. When the two layers have separated (emulsions are not formed), the aqueous layer is drawn off and the lead present is determined colorimetrically by the sulphide method.

If the aqueous solution still shows a pronounced red colour, it must be extracted once more with 15 c.c. of ether and 15 c.c. of amyl alcohol. A trace of red coloration may be ignored, as it is readily bleached on the addition of ammonia and potassium cyanide solution, and the small amounts of iron that are now present in no way interfere with the determination of the lead.

When more than 0·2 mgrm. of lead is present the ethereal solution in the separating funnel should be washed once with a few c.c. of very dilute nitric acid; this serves the double purpose of removing any of the aqueous phase adhering to the sides of the separator and of extracting any minute traces of lead thiocyanate dissolved by the ethereal layer. A blank experiment should be made on the reagents employed and the result deducted from the lead found.

To test the efficacy of the process, 5 grms. of lead-free salts were taken, and known amounts of lead nitrate and ferric chloride solution were added. The results are shown in the following table.

The blank on the reagents for both one and two extractions with the ethereal mixture was 0·02 mgrm., and this amount has been deducted in each instance from the lead found.

Compound	Ferric oxide added Mgrms.	Lead added Mgrm.	Lead found Mgrm.	Number of extractions
No salts	—	0·10	0·10	1
,,	5·0	—	Nil	1
Potassium chloride	5·0	0·10	0·09	1
Potassium nitrate	2·5	0·20	0·20	1
Ammonium sulphate	5·0	0·30	0·29	1
Ammonium nitrate	5·0	1·00	0·98	1
Sodium sulphate	25·0	0·15	0·15	2
Potassium chloride	12·5	1·50	1·53	2
Calcium nitrate	15·0	0·30	0·30	1
Magnesium nitrate	10·0	0·50	0·48	1
Ammonium sulphate	5·0	1·00	0·50	1

It will be seen that with ammonium sulphate containing 200 parts per million of lead only half the lead was found. This was due to the precipitation of lead sulphate, that is, to the inability of the ammonium sulphate to dissolve the lead sulphate. This defect may be remedied by working on a much smaller quantity of the sample.

Basic compounds, such as carbonates and oxides, can be tested for lead by dissolving 5 grms. in the minimum quantity of dilute nitric acid, making the volume up to 30 c.c., and continuing the process as detailed for water-soluble substances. If only the minimum quantity of nitric acid has been employed to obtain solution, 5 c.c. of 10 per cent. nitric acid should be added, as for soluble substances, but if excess of acid has been employed to obtain solution, the determination may be continued without the further addition of acid.

The process was tested in a similar manner to that used for water-soluble substances.

Compound	Ferric oxide added Mgrms.	Lead added Mgrm.	Lead found Mgrm.	Number of extractions
Sodium carbonate	15·0	0·20	0·19	2
Calcium hydroxide	5·0	0·10	0·10	1

APPLICATION TO ORGANIC COMPOUNDS.—After the destruction of a dyestuff or other organic substance by wet oxidation or by the Bang process, any iron in the resulting sulphuric acid solution may be removed by the following procedure:—The sulphuric acid solution is evaporated until only one or two c.c. of acid remain. This is diluted with 10 c.c. of water, 2 grms. of lead-free ammonium acetate are added, and then ammonia, until the solution is ammoniacal, and the liquid is boiled for 15 minutes or until it gives an acid reaction with litmus. Concentrated nitric acid is then added until the precipitated iron has re-dissolved, the solution is diluted with water to 30 c.c., and the thiocyanate separation process is employed. Where calcium phosphate is present in the solution after wet oxidation, 10 c.c. of the ammonium citrate solution described by Nicholls (ANALYST, 1931, **56**, 594) should be added after separation of the iron before applying the lead test; this will ensure the calcium phosphate remaining in solution during the test.

CALCIUM PHOSPHATE.—In the determination of lead in calcium phosphate by the process described by Nicholls (*loc. cit.*) the presence of traces of iron are objectionable, and Nicholls recommends preliminary treatment of the solution with sodium thiosulphate. The iron, however, may be separated by the thiocyanate method before the test for lead is applied: One grm. of calcium phosphate is dissolved in 3 c.c. of concentrated nitric acid and 17 c.c. of water, 5 c.c. of saturated ammonium thiocyanate solution are added, and the ferric thiocyanate is shaken out with ether and amyl alcohol. Thirty c.c. of Nicholls' ammonium citrate solution are then added, and the mixed solution is tested for lead by the sulphide method.

One grm. of iron-free calcium phosphate containing 30 parts per million of lead was mixed with 25 mgrms. of iron (added as ferric chloride) and 0·50 mgrm. of lead; the iron was completely extracted by two extractions, and the total amount of lead found was 0·5 mgrm.

FERROUS IRON.—Ferrous iron must be oxidised to the ferric state prior to the separation, by boiling the aqueous solution with 5 c.c. of 10 per cent. nitric acid; after cooling, the process is continued without further addition of acid.

By this process all the iron from a mixture of 0·350 grm. of ferrous ammonium sulphate, 5 grms. of sodium chloride and 0·30 mgrm. of lead was removed, without loss of lead, by two extractions.

INFLUENCE OF OTHER METALS.—Copper and bismuth, which are likely to occur as impurities in substances which may be tested by this process, yield coloured thiocyanates.

Copper.—Cupric ions yield a yellow thiocyanate which is partly extracted by a mixture of ether and amyl alcohol, but the colour remaining in the aqueous solution after extraction is instantly discharged on the addition of ammonia and potassium cyanide solution, and under these conditions the copper does not react with sulphide.

Bismuth.—Traces of bismuth in acid solution yield a characteristic yellow colour with ammonium thiocyanate, provided a large excess of this reagent is present. Bismuth thiocyanate may be extracted from an aqueous solution by the ether and amyl alcohol solvent, but, unfortunately, with the present mode of procedure the percentage of bismuth extracted depends largely on the nature of the salt under examination. Conditions for the separation, applicable to all compounds containing traces of bismuth, are in course of investigation.

I wish to thank Dr. A. M. Ward for his advice and helpful criticism.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE FLUORESCENCE ANALYSIS OF WAXES

FOR the examination of the fluorescence of waxes a K.B.B. quartz mercury vapour lamp and a Hanovia quartz mercury vapour lamp were used. The filters in both lamps had the same spectral characteristics, *viz.* all visible light was absorbed and a strong band of ultra-violet light between the limits of 3000 and 4000 Å with a maximum at 3660 Å was obtained.

English, foreign and white beeswax, Japan wax, Chinese wax, carnauba wax, commercial paraffin wax, yellow and white ceresin all gave characteristic fluorescences. Those waxes which were white in daylight showed a white fluorescence with blue or violet tones when examined under the lamp; the coloured waxes showed a fluorescence colour very similar to their colour in daylight.

With 50 per cent. mixtures of other waxes with English beeswax only, paraffin wax and carnauba wax were detectable under the lamp. Solutions in chloroform showed no fluorescence, except in the case of paraffin wax and carnauba wax; 10 per cent. of paraffin wax gave a milky yellowish-green fluorescing solution, and 10 per cent. of carnauba wax gave a solution with a strong bluish-white fluorescence. So strong is the fluorescence of carnauba wax that the addition of 1 per cent. to English beeswax is easily detectable in chloroform solution. By making standard samples containing known amounts of carnauba wax and dissolving 0·2 grm. of each in 100 c.c. of chloroform a good estimate of the amount of carnauba wax present in a suspected sample may be made.

J. A. RADLEY

THE ANALYTICAL CHARACTERISTICS OF COCONUT TODDY

In the manufacture of coconut toddy the sap is drawn from an unopened flower spathe of the coconut palm and collected in an earthenware vessel, which is placed over the end of the spathe. Tapping is usually carried out twice daily, and at each visit the chatty is emptied, a thin shaving is removed from the end of the spathe, and the earthenware vessel is replaced. The sap rapidly becomes infected with bacteria and yeasts, and the sugar present is soon converted into alcohol and acetic acid.

If it is desired to use the juice as a source of sugar instead of alcohol, a little milk of lime is placed in the earthenware vessel at the first tapping. This inhibits fermentation, and the liquid is evaporated to produce the brown sugar locally known as "*gula malacca.*" The non-sugar substances average about 12·5 per cent. of the total solids.

The following formula for calculating the original solids (mainly sugar) in the original sap from the percentages of alcohol and acetic acid in the toddy gives results very close to the truth:

Original solids = (alcohol by weight) × 2 + (acid as acetic acid) × 1·5 + extract. For morning toddies (*i.e.* tapped at 6.30 a.m.) the average value for original solids (S) was 18·7 per cent., with a variation from 17·0 to 20·1 per cent.; and for afternoon toddies (tapped at 2.30 p.m.), the average value was 18·3 per cent.

It was found that rainfall lowers the strength of toddy. For example, 96 per cent. of contractor's toddies taken in dry weather had an average strength (S) of 17·1 per cent.; whilst of those taken during a rainfall of less than 0·5 inch, the average strength was 16·7 per cent.

It is considered that the acidity of toddy cannot safely be regarded as a criterion of its age. Acidities of over 0·7 per cent. have been found in toddies which were undoubtedly fresh, and, on the other hand, toddies 66 hours old have given acidities of less than 0·6 per cent. In any case it would be expected that acidity would depend to some extent on the strength of the toddy, and should, therefore, be calculated as a percentage of the total original solids.

It is suggested that a better index of the age of a toddy is to be found in the extent to which fermentation has proceeded. In a stale toddy up to about 85 per cent. of the original solids may have fermented. In fresh toddies the degree of fermentation should not average more than 60 to 70 per cent., and in no individual sample should it have proceeded beyond 75 per cent., that is to say, at least 25 per cent. of its original solids should be unchanged.

Recommendations.—The present standards for toddy agreed upon by chemists in Malaya are based upon analyses made by Marsden in Kuala Lumpur in 1926. These standards require a minimum of 14 per cent. of original total solids, and an acidity calculated as acetic acid of less than 0·6 per cent. The present investigation has been carried out chiefly in order to discover what quality of toddy might reasonably be expected to be supplied to Government by a contractor, but it will also serve to provide a standard for toddy sold in non-government (or licensed) shops. It is suggested, therefore, that toddy drawn in dry weather from a considerable number of trees should, over a period of some months, reach an average strength of 17 per cent. of original total solids, and in no individual sample should this figure fall below 16 per cent. On the other hand, it may rise as high as 20 per cent.

Rainfall may have a considerable effect on the strength of toddies, and it is believed that this is due to water mechanically entering the collecting vessels. Where the rainfall during the period of collection does not exceed 0·5 inch its diluting effects are slight, and should not amount to more than about 5 per cent.

In such weather the average strength of toddies should not be less than 16·5 per cent., and no individual sample should fall below 15·5 per cent.

It is recommended that, so far as is possible, the sampling of toddy should be undertaken immediately after delivery by the contractor, and if it cannot be analysed immediately, it should be preserved by the addition of copper sulphate solution. According to experiments made in the Trade and Customs Laboratory in Kuala Lumpur, 20 drops of a saturated solution of copper sulphate will keep 300 c.c. of toddy unchanged for six months.

If samples of toddy must be taken some hours after delivery by the contractor, the degree of fermentation should not exceed 80 per cent.

It is further recommended that the collecting vessels should be of earthenware, and sufficiently wide in the mouth to be readily cleaned. They should be brushed out with a stiff wire brush after each tapping, and 5 to 10 per cent. of them should be replaced daily by vessels previously cleaned by immersion in boiling water. All other vessels, such as those used for carrying and mixing, should be of glazed earthenware or enamelled metal. Gourds should not be used.

It is clear that, if the above recommendations are to be carried out, toddy estates must be under continual supervision.

J. C. Cowap
F. H. Geake

Government Analyst's Department,
Straits Settlements

EXAMINATION OF UNREFINED SUGARS ON SALE IN VARIOUS HEALTH FOOD SHOPS

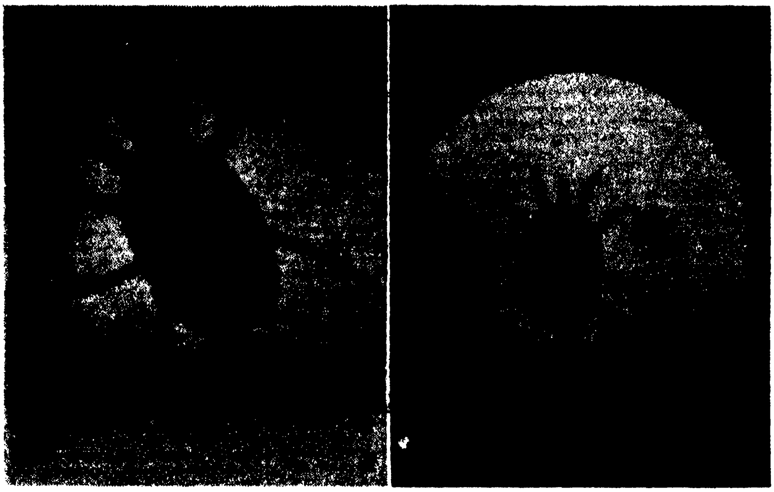
The samples purchased were apparently raw sugars or sugars boiled from unrefined syrups. Five samples, the colours of which ranged from yellow to dark brown, were tested.

	1	2	3	4	5
Moisture, per cent.	3·83	1·51	3·86	3·86	3·53
Ash, per cent.	2·34	1·36	2·29	2·29	2·38
Insoluble in boiling water, per cent.	0·98	0·82	0·64	0·82	0·96
Ash of insoluble matter, per cent.	0·56	0·40	0·32	0·44	0·56
Arsenic, parts per million	free	free	0·1	0·1	free
Sulphur dioxide, per million	240	60	200	200	200
Bacterial counts per grm. on agar media	2140	680	1860	1930	not tested

As the analyses show, these are very dirty raw sugars containing unusually high proportions of insoluble matter. The bacterial counts are very high, as are also the sulphite-contents. For some of these samples the content of sulphite is in excess of that legally permissible.

Another sample of unrefined sugar, purchased at a different shop, was found to be swarming with an incredible number of sugar acari. When about 10 grms. were shaken with about 200 c.c. of water until dissolved, and then allowed to stand, a film of wriggling acari, visible to the naked eye, was left on the surface. One sample of sugar contained 40 per grm.

Apart from these impurities, the high moisture-content makes these sugars unsound and most unfit for feeding children, for which purpose they are apparently recommended. Even if they have been dried, the coating of molasses on the sugar crystals renders them hygroscopic, and, in consequence, water is absorbed from the atmosphere as soon as an opportunity is found, and the packing material is unable to prevent it.



Viewed from above × 66. Underside × 28.

Sugar lice (*Carpoglyphus anonymus*) commonly but erroneously termed *Acarus sacchari*

H. C. Prinsen Geerligs in *Cane Sugar and its Manufacture* (p. 297–298) comments on this, and points out that the development of micro-organisms is thus promoted. Sugar is refined not solely for colour, as some would have us believe, but to make it a non-hygroscopic, sound food of exceptional chemical and bacteriological purity.

H. C. Siegfried de Whalley

Official Appointments

The Minister of Health has approved the following appointments:

Adrian J. C. Lickorish, F.I.C., as a Public Analyst for the County of Bedford, in addition to J. Kear Colwell (August 11th).

Frederick Dixon, B.Sc., F.I.C., as Public Analyst for the County of Stafford, in place of A. E. Johnson, and in addition to E. V. Jones (September 30th).

The Minister of Agriculture and Fisheries has approved the following appointments:

Frederick Dixon, B.Sc., F.I.C., as Deputy Agricultural Analyst for the County of Stafford, in place of A. E. Johnson (October 5th).

Eric Voelcker, F.I.C., as Deputy Agricultural Analyst for the County Borough of Oxford (October 5th).

Report of the Milk Products Sub-Committee to the Standing Committee on Uniformity of Analytical Methods

MILK PRODUCTS. REPORT No. 3

THE ANALYSIS OF SWEETENED CONDENSED MILK IN WHICH THE SUCROSE HAS ALTERED DURING STORAGE

THIS Sub-Committee was convened by the Standing Committee, and consists of the following members:—

Nominated by the Government Chemist: A. More, A.R.C.S., F.I.C.

Nominated by the London Chamber of Commerce: E. R. Bolton, F.I.C., M.I.Chem.E., A. L. Bacharach, B.A., F.I.C., *Ir.* W. J. Pelle, and J. Tavroges, B.Sc., A.I.C.

Nominated by the Manufacturing Confectioners' Alliance: T. Macara, F.I.C.

Nominated by the Society of Public Analysts and Other Analytical Chemists: G. D. Elsdon, B.Sc., F.I.C., E. Hinks, M.B.E., B.Sc., F.I.C. (*Chairman*), E. B. Hughes, M.Sc., F.I.C. (*Hon. Sec.*), A. E. Parkes, F.I.C., and J. D. Roberts, B.Sc.

In previous reports (*Milk Products: Report No.* 1, p. 2, ANALYST, 1927, **52**, **403**; *Report No.* 2, "The Determination of Sucrose in Sweetened Condensed Milk," p. 10, ANALYST, 1930, **55**, 120) it was recommended that for the purpose of the Public Health (Condensed Milk) Regulations the percentage of total milk solids should be determined by subtraction of the percentage of sucrose from that of total solids.

Such a procedure is admissible only when no material alteration has taken place in the sucrose, and the recommendation in *Report No.* 2 contained the proviso "it being understood that the sample is a product prepared from milk and sucrose only, and that it is in sound normal condition." If any of the sucrose has been hydrolysed, or has undergone other change, total milk solids will be in error, any non-volatile derivative of sucrose being wrongly credited to milk solids.

The present Report (No. 3) deals with certain decomposition products of sucrose, their influence, if present, upon the determination of total milk solids as described in *Report No.* 2, and the means to be adopted in order to obtain the correct figure for total milk solids. As will appear later, the total milk solids figure is not the only one to be affected by breakdown of the sucrose: if decomposition has proceeded in a certain direction, the figure obtained for the remaining sucrose, as determined by the polarisation process, is also affected.

Work on the matter which is the subject of this Report was begun in March, 1930. The problem to be solved was found to require the devising of new processes rather than the examination of established processes and selection of the best.

The work carried out by the Committee can be divided into three stages:

(i) Investigation of methods of determining small amounts of invert sugar in sweetened condensed milk.

In the course of this work it was discovered that the change which occurs in the sucrose on keeping sweetened condensed milk does not usually result in the presence of invert sugar, as such, but that the laevulose fraction appears, in part, as laevan.

(ii) The second stage of the work involved the study of this change, and the elaboration of methods for determining the products of the change, so that the sucrose originally present could be calculated.

(iii) The third stage developed into a simplification of Stage (ii), *i.e.* the development of a direct method which admits of a determination of the amount of sucrose originally present, without carrying out the more lengthy procedure of Stage (ii), which, however, remains essential as affording an explanation of the change, and providing, if necessary, a confirmation of the result obtained by the simplified process.

(I) GENERAL

The problem was viewed at first as being one solely of the detection and determination of invert sugar, and processes were developed accordingly. During the course of this work, however, the observation was made that in a sweetened condensed milk, in which the sucrose had been altered by prolonged storage, the "apparent lactose," as determined by chloramine-T-iodide oxidation,[1] was higher than when determined by copper reduction; if invert sugar had been present the reverse should have been the case, since chloramine-T-iodide does not oxidise laevulose. The only explanation of this observation appeared to be that, assuming dextrose and laevulose to be present, the dextrose exceeded the laevulose in amount, but at the time there was no means of confirming this.

Later, on application of the Hinton and Macara process for the direct determination of laevulose[2] to a sweetened condensed milk, which had undergone extensive alteration on keeping, it was found that, although between 8 per cent. and 9 per cent. of sucrose had disappeared, only about 0·5 per cent. of laevulose was present, whilst chloramine-T-iodide oxidation again pointed to excess of dextrose over laevulose.

These perplexing results were eventually found to be due to the formation of laevan.

Nascent laevulose from sucrose is known to be condensed to laevan, a gum,[10] by the action of the levanase of certain micro-organisms, 9 parts by weight of laevan being formed from 10 parts of laevulose. From a sweetened condensed milk which, after storage, exhibited this excess of dextrose over laevulose, a laevan-forming organism was isolated and grown in pure culture. A preparation of laevan was made from a sucrose-peptone solution in which this organism was allowed to grow. This laevan was precipitated by 86 per cent. alcohol, washed with alcohol and ether, and dried. It was free from dextrose and laevulose, and its $[\alpha]_D^{20}$ was found to be $-50°$, calculated on the dry ash-free material.

Laevan does not reduce cupric reagents and is less laevo-rotatory than laevulose. On treatment with acids (as, for instance, in the inversion process for the determination of sucrose), laevan is hydrolysed quantitatively to laevulose.

Formation of laevan thus introduces considerable complication into the analysis of a sweetened condensed milk. In the first place, the copper-reducing power of the serum is diminished proportionately to the amount of laevan formed; secondly, the rotatory power of the serum is affected; and, thirdly, when the serum is inverted, for the determination of sucrose, the laevulose is re-constituted from the laevan and exhibits the same rotatory power and the same copper-reducing power as it would have done if no condensation to laevan had taken place.

The optical rotation and the copper-reducing power of the "inverted" serum are, therefore, the same whether invert sugar has, or has not, been formed from the sucrose, and whether laevan has, or has not, been formed either directly from the sucrose or from the laevulose fraction of invert sugar; they are the same as would have been shown by the inverted serum of the freshly prepared milk before any alteration in the sugars had taken place, provided that formation of invert sugar, or of laevan, laevulose and dextrose accounts for the whole of the altered sucrose. The optical rotation and copper-reducing power of the "uninverted" serum are, on the contrary, affected according to the extent of laevan formation. Thus, when laevan is formed, not only is the determination of altered sucrose affected, but the method for the determination of the remaining sucrose recommended by the Committee (*Report No.* 2) is invalidated, as would be any method depending upon acid inversion, whether by polarisation or by copper reduction.

It is clear, therefore, that it is of prime importance to ascertain, in any given case, first, whether any alteration of the sucrose has taken place; and secondly, whether the altered sucrose appears in the form of invert sugar or in that of a mixture of dextrose, laevulose and laevan.

From the examination of a number of old sweetened condensed milks (which had been kept in their original sealed containers) it would appear that formation of dextrose and laevulose, with condensation to laevan of a considerable proportion of the laevulose, is the usual direction in which sucrose is altered in those cases where any alteration at all has taken place. The analogous formation of dextran, by condensation of dextrose, has not been observed, though such a possibility should be borne in mind. It is important to note that no evidence was found of any alteration in the lactose, even in an extreme case in which nearly 9 per cent. of sucrose, as such, had disappeared, with the formation of much laevan.

The possible presence of invert sugar, of dextrose and of laevan, must, then, be taken into account in any critical analysis of sweetened condensed milk.

In considering a scheme for such an analysis, it is convenient to approach the more complicated issue of laevan through the simpler one of invert sugar.

In a mixture of lactose, sucrose and invert sugar, all these should be determinable by a combination of polarimetric and suitable copper-reduction methods. The heating of milk, however, has a considerable effect upon the specific rotation, and some effect on the copper-reducing power, of lactose. Though the temperature to which the milk is exposed during the manufacture of *sweetened* condensed milk does not appear to be high enough to have any significant effect, the uncertainty attaching to this renders the determination of doubtful accuracy for small amounts of invert sugar.

(II) COLORIMETRIC DETERMINATION OF INVERT SUGAR

Some success was obtained with a direct qualitative and quantitative colorimetric process based upon the destruction of lactose by the method of Kruisheer[3] and the colorimetric method of Kolthoff.[4] It was found that by chloramine-T-iodide oxidation of the serum (prepared by phosphotungstic acid clarification) lactose and dextrose could be eliminated and the laevulose determined colorimetrically by an alkaline 3-5-dinitro-salicylic acid reagent. This method was abandoned in favour of more satisfactory methods devised later.

(III) THE BARFOED REAGENT

Monier-Williams,[5] in a Report published by the Ministry of Health, has worked out an application of Barfoed's solution (copper acetate and acetic acid) to the detection and determination of invert sugar in sweetened condensed milk. This method has been fully studied by the Committee, and in a modified form has supplied the basis of one of the processes recommended in this Report.

(IV) MODIFICATION OF THE BARFOED REAGENT AND PROCESS

When a mixture of Barfoed's solution and serum prepared from sweetened condensed milk is heated, reduction readily takes place if invert sugar is present. Even in the absence of invert sugar, however, a noticeable amount of reduction takes place, increasing steadily with the time of heating. Monier-Williams attributes this to hydrolysis of the sucrose by the acetic acid, but the Committee finds that the lactose in the serum has a considerable reducing action upon Barfoed's solution.

In the method described in the Ministry's Report[5] a fresh milk serum, containing sucrose, is used as a control, the reaction in the two serums—the one under examination and the control—being stopped when the control begins visibly to reduce the copper. The lactose effect is, however, sufficiently powerful to necessitate equal concentrations of lactose in the serum under examination and in the control serum. Variation in the proportion of lactose in condensed milk, and in fresh milk, may be so large as to render any one fresh milk uncertain as a control for a given condensed milk.

Attempts were made to destroy the invert sugar in one portion of the condensed milk serum by preliminary heat treatment with the Barfoed reagent, and to use the resulting serum (after filtration) as the control, thus ensuring an approximately equal concentration of lactose in the control. This procedure did not give satisfactory results, as the reducing power of the serum was greater after the preliminary treatment than before.

In order to overcome these defects in the Barfoed method under discussion, experiments were made with the object of minimising the reducing action of lactose, and so avoiding the necessity for the fresh milk control.

It was found that by modifying the composition of the copper acetate solution, by reducing the temperature, and by limiting and fixing the time for the reduction, the reducing action of lactose, and of a milk serum free from invert sugar, could be rendered negligible, while at the same time the reducing action of invert sugar could be maintained.

First, the addition of sodium acetate to the Barfoed reagent effects an improvement and causes the reduction to become more nearly a linear function of the amount of invert sugar present. This effect is not due to buffering of the reagent by the sodium acetate, for determination of its neutralisation curve shows that true buffering does not occur.

Secondly, the rate at which sugars reduce cupric solutions depends, for a given type of reagent, upon the acidity or alkalinity of the solution and also upon temperature. Application of these principles enabled further improvement in the selective action of a Barfoed reagent to be effected.

Moreover, laevulose and dextrose are not equally reactive to Barfoed's solutions, the reduction by laevulose being the greater. By varying the proportion of acetic acid (in the presence of sodium acetate) the relative reducing powers of these two sugars may be altered. Diminishing the acetic acid causes their reducing powers to approach equality, but when this point is reached the lactose effect becomes unduly high. A compromise has, therefore, to be adopted.

The reduced copper is best determined by the Bertrand procedure (solution in acid ferric sulphate solution and titration of the reduced iron with standard permanganate solution), and is conveniently expressed in terms of $N/10$ potassium permanganate solution.

Table I shows the effect of varying the proportions of sodium acetate and acetic acid. All the reagents contained about 50 grms. of crystallised copper acetate per litre, the crystallised sodium acetate and acetic acid being varied as shown in this table. 70 ml. of the reagent and 25 ml. of a sweetened fresh milk serum,* alone and also with the addition of 1 ml. of a 2·5 per cent. solution of dextrose or laevulose, were immersed in a bath at 80° C. for 20 minutes.

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* In these and subsequent experiments a sweetened fresh milk serum was prepared to simulate the serum of sweetened condensed milk by zinc acetate and potassium ferrocyanide clarification, as described in Appendix I, 100 grms. of fresh milk and 16 grms. of sucrose being used instead of the 40 grms. of sweetened condensed milk.

TABLE I

Reagent	Sodium acetate Grms. per litre	Acetic acid Ml. per litre	Serum alone	Serum *plus* 25 mgrms. of dextrose	Serum *plus* 25 mgrms. of laevulose
			$N/10$ potassium permanganate solution Ml.	Ml.	Ml.
1.	40	2	3·1	10·2	11·3
2.	40	4	1·0	10·3	11·35
3.	40	8	0·2	2·8	7·2
4.	80	4	0·75	10·15	11·25
5.	80	6	0·2	8·8	10·65
6.	80	8	0·1	6·6	9·3
7.	80	12	0·15	1·15	6·9
8.	60	6	0·15	8·7	10·7
9.	60	8	0·1	7·3	10·0
10.	60	10	0·15	5·25	8·75

Reagent 8 was adopted as being the most suitable; at 80° C. the lactose effect is negligible, whilst the dextrose and laevulose effects are maintained at a high level. This reagent is hereinafter referred to as *Modified Barfoed reagent.*

The reaction, at the point at which the reducing action of lactose is negligible but at which laevulose and dextrose react sufficiently rapidly, is very sensitive to temperature, and, to a less extent, to time. The effect of temperature on the extent of the reduction by sweetened fresh milk serum is shown in Table II.

TABLE II

70 ml. Modified Barfoed solution *plus* 25 ml. of sweetened fresh milk serum. Time of heating: 20 minutes.

Temperature ° C.	$N/10$ potassium permanganate solution Ml.
78	0·1
80	0·2
82	0·8

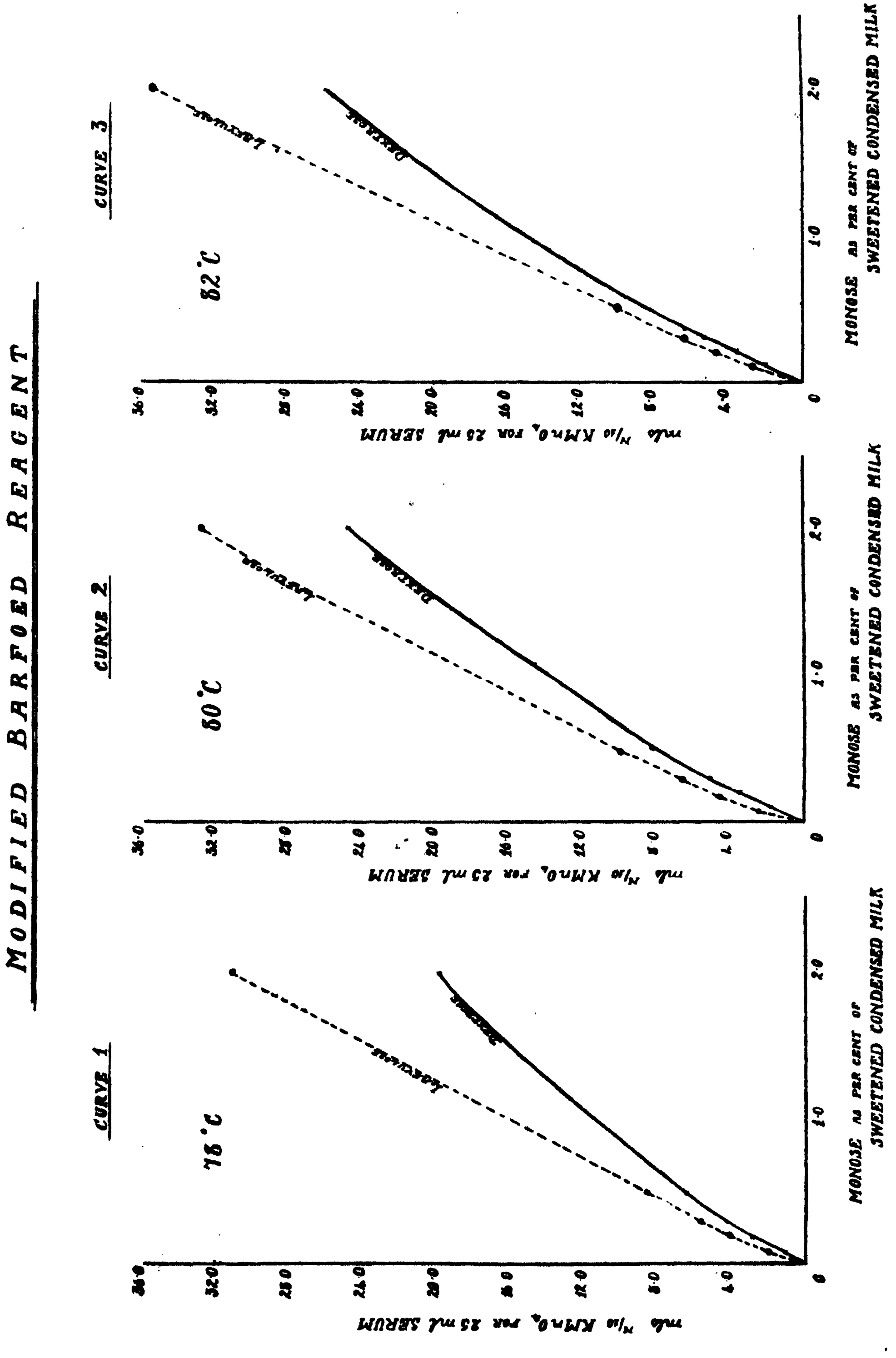
The following curves show the reducing actions of laevulose and dextrose on the Modified Barfoed reagent at various concentrations and at three temperatures. The monose sugar was dissolved in 25 ml. of sweetened fresh milk serum.

In Table III are given the results obtained with the Modified Barfoed reagent for laevulose, dextrose and invert sugar, the sugars being expressed as percentages of a sweetened condensed milk of ordinary composition; for the experiment these reducing sugars actually were added to 25 ml. of a sweetened fresh milk serum.

TABLE III

Temperature 80° C.; time of heating: 20 minutes.

Monose sugar as per cent. of condensed milk Per Cent.	$N/10$ potassium permanganate solution for Laevulose Ml.	Dextrose Ml.	Invert sugar Ml.
Nil	0·15 (blank)	0·15 (blank)	0·15 (blank)
0·1	3·50	2·7	2·8
0·2	5·50	4·75	4·25
0·3	7·35	6·0	6·15
0·5	11·55	8·75	9·85
1·0	19·50	15·45	18·0
2·0	34·05	25·35	29·45



MODIFIED BARFOED REAGENT

The most favourable conditions are:—

(i) Heating in a large water-bath maintained at 80° C.
(ii) Allowing the reaction to proceed for 20 minutes.

Under these conditions a sweetened fresh milk serum has a negligible reducing action. Owing, however, to the sensitiveness of the reaction to temperature, and also to a slight difference in reactivity of different preparations of the reagent, precise quantitative relations cannot be assumed from the above tables and curves. For accurate work it is necessary to standardise the reagent by using control serums containing approximately the same proportions of sugars as the serum under examination, the controls being heated in the same bath as the serum being tested.

By the use of this Modified Barfoed solution as little as 0·1 per cent. of invert sugar, of dextrose or of laevulose in a condensed milk may readily be detected. Obviously the process will not indicate which of these sugars is present, and a knowledge of the amount of either the laevulose or dextrose is necessary in order to interpret, quantitatively, the reduction obtained.

The process has been of great service in establishing the nature of the changes occurring in the sucrose of sweetened condensed milk (as will appear later), and it takes its place in the recommendations of the Committee in this Report, as providing a means of detecting whether or not any significant change has taken place in the sucrose.

(V) INVERT SUGAR BY DIRECT DETERMINATION OF LAEVULOSE

Hinton and Macara[2] have developed a process for the determination of laevulose in sweetened condensed milk. It was intended to make this process the basis for the determination of invert sugar, and, if invert sugar were the only hydrolysis product of sucrose present, the process would be perfectly valid.

The application of this and of the chloramine-T and the Modified Barfoed processes to samples of altered sweetened condensed milk, however, demonstrated that the products of the altered sucrose were not dextrose and laevulose in equal proportions, the dextrose being invariably in excess, and it is, therefore, inadmissible to infer the amount of dextrose from a determination of the laevulose. Further investigation, by means of the polarimetric readings combined with chloramine-T titrations on the serum before and after inversion, indicated that some substance was present which was neither dextrose nor laevulose, but which was converted into one of these during the inversion process. This substance, as stated earlier, proved to be laevan. Consequently, neither the Modified Barfoed nor the Hinton and Macara process can be used by itself to determine the amount of altered sucrose. Nevertheless, the determination of laevulose by the latter process is necessary in the analysis of these altered samples when their detailed composition is required. This process has, therefore, been closely studied by the Committee.

In the following table are given the results obtained in a series of analyses by this process by members of the Committee (A–H), using sweetened condensed milk from various sources, with the addition of known quantities of invert sugar.

TABLE IV

Laevulose (added as invert sugar) as per cent. of condensed milk	Laevulose found Per Cent.							
	A	B	C	D	E	F	G	H
0·05	0·06	0·06	0·06	—	0·06	0·06	0·03	0·06
0·1	0·10	0·10	0·10	0·10	0·11	0·11	0·11	0·11
0·25	0·26	0·27	0·26	0·26	0·26	0·25	0·26	0·26
0·5	0·52	0·55	0·50	0·52	0·52	0·54	0·51	0·53
0·6	—	—	—	—	0·60	—	—	—
1·0	1·00	1·00	0·99	1·10	1·02	1·06	0·91	1·03

This process has been much used by the Committee during their investigations, and is recommended as quite satisfactory for the determination of laevulose. Full details of the process are given in Appendix III.

(VI) SUGARS AND LAEVAN BY THE MODIFIED BARFOED REAGENT

As it appeared that, in the altered sweetened condensed milks examined by the Committee, a portion of the sucrose had been changed to dextrose, laevulose and laevan, it was, at first, thought to be necessary, in order to ascertain the proportion of total milk solids, to determine the various sugars and laevan. This was first attempted by use of the Modified Barfoed reagent, in combination with the direct determination of laevulose and the determination of the specific rotation before and after inversion. The application of this method is best explained by means of an example.

The amount of laevulose in the condensed milk serum (20 per cent.) was determined by the Hinton and Macara process, and the serum was tested against a standard prepared by adding dextrose and laevulose to sweetened fresh milk serum. The amount of laevulose so added was arranged to be the same as that present in the condensed milk serum, and the dextrose added was in the neighbourhood of the amount expected in the unknown.

The mixtures tested by the Modified Barfoed procedure were:—

(1) 4 ml. condensed milk serum (this contained 0·0120 grm. laevulose).

(2) 4 ml. sweetened fresh milk serum containing 0·0120 grm. laevulose and 0·0380 grm. dextrose.

(3) 4 ml. sweetened fresh milk serum.

The titrations of the reduced copper were:—

(1) 16·95 ml.; (2) 16·75 ml.; (3) 0·3 ml. of $N/10$ permanganate solution.

Hence the net amounts due to laevulose and dextrose were:—(1) 16·65 ml.; (2) 16·45 ml.

The laevulose in both of these solutions was the same in amount; hence, since the titrations were so close, the relative proportions of the dextrose and laevulose must have been very similar in both cases, and it is sufficiently accurate to assume that the *total* amounts of the two sugars were directly proportional to the respective titrations. [Had the titrations lain further apart, then for strict accuracy it would have been necessary to repeat the test with a more suitable amount of added dextrose in (2).]

The total dextrose and laevulose in (2) being 0·0500 grm., the total in (1) is therefore

$$0{\cdot}0500 \times \frac{16{\cdot}65}{16{\cdot}45} = 0{\cdot}0505 \text{ grm.}$$

But of this, 0·0120 grm. is laevulose; therefore the amount of dextrose is 0·0385 grm., and the percentage of dextrose in the sample is

$$0{\cdot}0385 \times \frac{100}{4} \times \frac{100}{20} \times 0{\cdot}9714^{*} = 4{\cdot}67 \text{ per cent.}$$

The laevulose is 1·45 per cent. (direct determination). Hence, the laevulose, converted into laevan, is 4·67 − 1·45 = 3·22 per cent., and the laevan so formed is 3·22 × 0·9 = 2·90 per cent.

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* Volume of precipitate correction; the specific rotations given in this example are corrected for volume of precipitate.

The amount of sucrose present as such can obviously be determined if we subtract from the direct polarisation reading the rotations due to the laevan, laevulose and dextrose, and, from the invert polarisation reading, that due to the inversion products derived from these substances.

The values taken in this example for the specific rotations of dextrose, laevulose and laevan are corrected, as far as is possible from available data, for concentration, effect of acid and salts, etc.

$$\begin{array}{lrl}
\text{The part of the direct } [\alpha]_D^{20} \text{ due to dextrose} & = +52{\cdot}7 \times \frac{4{\cdot}67}{100} & = +2{\cdot}46^\circ \\
\text{,, ,, ,, ,, ,, ,, ,, ,, laevulose} & = -93{\cdot}0 \times \frac{1{\cdot}45}{100} & = -1{\cdot}35^\circ \\
\text{,, ,, ,, ,, ,, ,, ,, ,, laevan} & = -50 \times \frac{2{\cdot}90}{100} & = -1{\cdot}45^\circ \\
\hline
 & \text{Net effect} & -0{\cdot}34^\circ
\end{array}$$

The actual direct $[\alpha]_D^{20}$ was + 29·75°, and the direct $[\alpha]_D^{20}$ thus amended is, therefore, +30·09°.

In the inverted solution, the part of the $[\alpha]_D^{20}$ due to these three constituents is the rotation of an amount of invert sugar equal to twice the amount of the dextrose, that is,

$$-20{\cdot}85 \times \frac{9{\cdot}34}{100} = -1{\cdot}95^\circ$$

The actual invert $[\alpha]_D^{20}$ was —1·59°, and the amended invert $[\alpha]_D^{20}$ is, therefore, +0·36°.

The sucrose present is then given by the change of $[\alpha]_D^{20}$ on inversion, divided by the inversion divisor factor 0·8825; thus sucrose

$$= \frac{30{\cdot}09 - 0{\cdot}36}{0{\cdot}8825} = 33{\cdot}68 \text{ per cent.}$$

The analysis thus gives:—

Sucrose	..	33·68 per cent.
Laevulose	..	1·45 ,, ,,
Dextrose	..	4·67 ,, ,,
Laevan	..	2·90 ,, ,,

(VII) SUGARS AND LAEVAN BY CHLORAMINE-T TITRATION

On inversion of the condensed milk serum, laevan is hydrolysed to laevulose, whilst dextrose and laevulose are unaffected. By determination of the specific rotation and of the chloramine-T titration, both before and after inversion, combined with a direct determination of the laevulose, the amounts of all sugars and laevan can be calculated. This method, again, is best explained by an illustrative example.

The particular milk, the analysis of which is here recorded, was at least two years old. The analysis was conducted as follows:—

Polarisation by the Committee's *Report No.* 2 method, with zinc clarification.

$[\alpha]_D^{20}$ *Direct* + 29·75° (corrected for volume of precipitate)
Invert — 1·59° (,, ,, ,, ,, ,,)

Laevulose by direct determination.

1·45 per cent. (corrected for volume of precipitate).

Chloramine-T titrations. A 20 per cent. serum, prepared by phosphotungstic acid clarification, was diluted to 4 per cent.

Direct. Twenty ml. of this 4 per cent. serum taken for titration.
Chloramine consumed (as $N/20$ thiosulphate) 23·67 ml.

Invert. Forty ml. of 4 per cent. serum inverted, neutralised and made up to 100 ml.; 20 ml. of this taken for titration.
Chloramine consumed (as $N/20$ thiosulphate) 22·25 ml.

CALCULATION OF TRUE LACTOSE AND ORIGINAL SUCROSE.*

From the "invert" titration:

The correction for the effect of inversion, etc., on lactose and other milk constituents (see Section VIII) = 0·15 ml. in this case.

Hence the iodine equivalent to the lactose *plus* inverted sucrose, is

$$(22{\cdot}25 - 0{\cdot}15) \times 0{\cdot}006346 = 0{\cdot}14025 \text{ grm.},$$

or, expressed as per cent. of the sample, 42·89 per cent. (corrected for volume of precipitate).

The iodine equivalents of lactose hydrate and invert sugar under the conditions of this titration (see Tables XIII and X of the original paper[1]) are 0·701 and 0·705, respectively.

If L and S be the percentages of lactose hydrate and of sucrose in the milk before any alteration, then for the fully inverted solution:

$$0{\cdot}701\,L + (0{\cdot}705 \times 1{\cdot}053\,S) = 42{\cdot}89$$

Also, from the invert polarisation:

$$0{\cdot}524\,L - 0{\cdot}2195\,S = -\,1{\cdot}59,\dagger$$

and from these two equations

$$S = 43{\cdot}47, \text{ and } L = 15{\cdot}15.$$

Sucrose present at the time of analysis.—The "invert" chloramine titration, corrected as above mentioned, is 22·10 ml. Then the sucrose present is calculated from the difference in thiosulphate titrations before and after inversion, thus

$$\frac{\left(22{\cdot}10 \times \frac{100}{40} - 23{\cdot}67\right) \times 0{\cdot}006346}{0{\cdot}741} \times \frac{100}{0{\cdot}8} \times 0{\cdot}9786 = 33{\cdot}09$$

(0·9786 being the volume of precipitate correction, $\frac{100}{0{\cdot}8}$ the factor converting 20 ml. of the solution titrated into 100 grm. of sample, and 0·741 the sucrose factor taken from Table XV[1]).

Note.—The dilutions and amounts taken for the chloramine titrations are not identical with those used for unchanged condensed milk as in the published process[1]; they had to be arranged so as to give suitable titrations in view of the extra reducing sugar present. It is desirable to have the "direct" not very different from the "invert" titration. It sometimes happens, as in this case, that the titrations fall somewhat outside the range of the tables of factors given in the published paper; slight extrapolation is then required, and is permissible.

---

* The term "original sucrose" means the sucrose in the condensed milk before any alteration had taken place.

† See Section (VIII) formula (2).

Apparent Lactose.—From the "direct" titration a small correction has to be deducted for the slight absorption of iodine by the sucrose (see Table XIV of the original paper). In the present case this is 0·09 ml., and the corrected titration difference is thus 23·58 ml.

Then the "apparent lactose" is

$$\frac{23{\cdot}58 \times 0{\cdot}006346}{0{\cdot}700} \times \frac{100}{0{\cdot}8} \times 0{\cdot}9786 = 26{\cdot}15 \text{ per cent.}$$

Dextrose.—The difference between the true and apparent lactose (26·15—15·15 =11·00) represents the dextrose, expressed as lactose hydrate. Since dextrose has just twice the iodine-reducing power of lactose hydrate, the actual percentage of dextrose is, therefore, 5·50.

Laevan.—The difference between the dextrose and laevulose gives the amount of the latter which has been condensed to laevan, which is, therefore,

$$0{\cdot}9 \times (5{\cdot}50 - 1{\cdot}45) = 3{\cdot}65 \text{ per cent.}$$

The full analysis thus gives:

	Per Cent.
Sucrose	33·09
Lactose (anhydrous) ..	14·39
Laevulose	1·45
Dextrose	5·50
Laevan	3·65

It will be observed that this scheme of analysis gives the lactose, and is thus a more complete scheme for the determination of all sugars present than that described under Section VI, though the latter has the advantage of providing a direct demonstration of the presence of reducing sugars other than lactose.

As the result of various analyses carried out as above, it became clear that by polarimetric and chloramine-T determinations, using inverted serum, it was possible to arrive at the amount of sucrose originally present in the milk. This being so, a detailed determination of the various sugars and laevan is not necessary for the purpose of determining the percentage of milk solids. A simplified method of determining the original sucrose is given in the following Section (VIII), but where a determination of the various sugars and laevan is desired, the most suitable scheme available is that described in this section (VII).

(VIII) DETERMINATION OF ORIGINAL SUCROSE* BY POLARIMETER AND CHLORAMINE-T-IODIDE OXIDATION

When sucrose, which has become partly altered to dextrose, laevulose and laevan (or to invert sugar), is inverted, the product is invert sugar only, and in the same quantity as would have been given by the original sucrose, had none undergone alteration. Consequently, after inversion of the sucrose of a sample of sweetened condensed milk the sugars in solution are lactose and invert sugar; and these two may obviously be determined by calculation from the results of two independent quantitative measurements of these two sugars, *e.g.* by polarisation and measurement of reducing power towards copper or iodine (using chloramine-T). Examples of analyses by polarisation and copper-reducing power of the inverted serum are given later (see Table VII). The Committee found, however, the most suitable and reliable reduction method to be the chloramine-T method.

This method was studied by the Committee during the preparation of *Report No.* 2, and was then found to give slightly higher results for sucrose than those obtained by the polarimetric method recommended in that report, the accuracy of which, in the absence of hydrolysis products, was fully established. It has since been found that this error is due to a slight absorption of iodine by non-sugar constituents of the *inverted* milk serum, as shown by experiments carried out on the following lines:—

---

* See footnote, Section VII, page 639.

Sweetened fresh milk serum* containing a known amount of sucrose and, also, sucrose mixed with clarified fresh milk, were subjected to the chloramine-T process before and after inversion. In the absence of any effect produced by the milk serum constituents, the amount of reagent absorbed in the inverted solution should be the sum of the amount used in the uninverted solution, due to lactose, *plus* the amount, calculated from the tables in the paper[1], due to the inverted sucrose. This, however, was found not to be the case, the results obtained from the inverted solutions being invariably higher by a small amount. The discrepancy was found to vary directly with the proportion of milk solids in the serums, the absorption of iodine by the non-sugar, non-precipitated milk constituents being found to be equivalent to 2·2 ml. *N*/20 thiosulphate solution per 1 grm. of fat-free milk solids.

Hence, it is possible to apply a correction to the titration results on the inverted serum to compensate for this effect. In the analysis of a condensed milk by the chloramine-T method, the amount of fat-free milk solids represented by the quantity of serum taken in the test is approximately 0·07 grm., and the correction to be applied to the titration is, therefore, 0·15 ml. *N*/20 thiosulphate solution. If other dilutions are taken, or abnormal samples (as regards fat-free solids) are in question, this figure can be adjusted to accord with the amount of fat-free solids corresponding to the volume of serum taken.

When this correction is applied, the chloramine-T method gives the true sucrose. In the following table is given the analysis of a fresh sweetened condensed skim milk:

TABLE V

	Per Cent.
Sucrose by chloramine-T process	43·40
Lactose (anhydrous)	14·88
Dextrose	0·01
Laevulose	0·02

Direct $[\alpha]^{20}_{D}$ calculated $+ 36{\cdot}96^\circ$

Do. $[\alpha]^{20}_{D}$ found $+ 37{\cdot}05^\circ$.

Sucrose by Committee's *Report No.* 2 method, 43·40.

Directions for the process are given in Appendix IV. The derivation of formulae there employed is as follows:—The serum prepared by zinc acetate and potassium ferrocyanide clarification is a 20 per cent. solution of the condensed milk; this becomes a 16 per cent. solution after inversion. A suitable dilution of this serum is 20 ml. made up to 250 ml., of which 25 ml. is taken for chloramine-T titration. The phosphotungstic clarification is, however, to be preferred for the chloramine-T process, and for this a 5 per cent. solution of condensed milk is clarified; 25 ml. of this are inverted and made up to 100 ml. Twenty-five ml. of this dilution are taken for the chloramine-T titration (in both cases the dilutions must be neutralised as described in Appendix IV).

Let $R = [\alpha]^{20}_{D}$ of the inverted solution (zinc clarification);
E = grms. of iodine consumed by 100 grms. of sample after inversion;
n = titration-difference in ml. *N*/20 thiosulphate.
V = volume in ml. to which the sample is diluted before filtration;
v = correction in ml. for volume of precipitate produced during clarification.

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* See footnote, page 633.

(The titration-difference (n) has to be corrected for absorption by non-sugars; this correction, as shown above, is usually $-0{\cdot}15$ ml.)

$$\text{Then E (zinc serum)} = (\text{n} - 0{\cdot}15) \times 0{\cdot}006346 \times \frac{250}{25} \times \frac{100}{20} \times \frac{100}{16} \times \frac{\text{V}-\text{v}}{\text{V}}$$

$$= (\text{n} - 0{\cdot}15) \times \frac{63{\cdot}46}{32} \times \frac{\text{V}-\text{v}}{\text{V}}$$

and E (phosphotungstic acid serum)

$$= (\text{n} - 0{\cdot}15) \times 0{\cdot}006346 \times \frac{100}{25} \times \frac{100}{25} \times \frac{100}{5} \times \frac{\text{V}-\text{v}}{\text{V}}$$

$$= (\text{n} - 0{\cdot}15) \times 63{\cdot}46 \times 0{\cdot}032 \times \frac{\text{V}-\text{v}}{\text{V}}$$

Now, with the dilutions suggested, the factors for lactose hydrate and invert sugar (1·053 × sucrose), in grms. of iodine per 1 grm. of sugar, are 0·702 and 0·706, respectively.

Hence, if L and S be the percentages of lactose hydrate and of original sucrose, respectively, we have

$$0{\cdot}702\,\text{L} + 0{\cdot}706 \times 1{\cdot}053\,\text{S} = \text{E}. \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

The specific rotations $[\alpha]^{20}_{\text{D}}$ in the inverted zinc serum of lactose hydrate and of inverted sucrose are 52·4° and −21·95°, respectively. Hence

$$0{\cdot}524\,\text{L} - 0{\cdot}2195\,\text{S} = \text{R}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

From equations (1) and (2)

$$\text{S} = 0{\cdot}964\,\text{E} - 1{\cdot}29\,\text{R} \text{ and } \text{L} = 0{\cdot}404\,\text{E} + 1{\cdot}37\,\text{R}$$

Thus from the two operations of determining the specific rotation and the chloramine-T titration of the inverted solution the percentage of original sucrose is obtained.

Chloramine-T titrations obtained on the zinc clarified serum tend to be a little low. This appears to be connected with the precise conditions of alkalinity. As this difficulty does not occur with the phosphotungstic clarified serum, the latter is advised, though the zinc clarified serum can be used as a preliminary if desired.

TESTS OF THE PROCESS ON OLD CONDENSED MILKS.—*Report No.* 2[6] (Tables II and III) contains the results of analyses by members of the Committee of samples of specially prepared condensed milk. These analyses were made in November and December, 1929. One tin of each of these batches was reserved, and in March, 1932, was analysed by the above method, with the following results:

A. *Table II Milk.*

Appearance on opening: Normal.

Polarisation. Direct $[\alpha]^{20}_{\text{D}}$ on sample + 34·28°.
Invert $[\alpha]^{20}_{\text{D}}$ „ „ − 3·15°.

Original sucrose from invert polarisation and chloramine-T (both on zinc serum)	42·39 per cent.
Average figure as published in *Report No.* 2 for sucrose	42·54 per cent.

Note.—Very little alteration of the sucrose had taken place in this milk.

B. *Table III Milk.*

Appearance on opening: Showed brownish discoloration and thickening.

Polarisation. Direct $[\alpha]_D^{20}$ on sample + 33·93°.
Invert $[\alpha]_D^{20}$ „ „ − 2·32°.

Original sucrose from invert polarisation (zinc clarification) and chloramine-T (phosphotungstic clarification)	44·56 per cent.
Original sucrose from invert polarisation and chloramine-T (both zinc clarification)	44·16 per cent.
Average figure as published in *Report No.* 2 for sucrose	44·52 per cent.

Note.—The polarisation in March, 1932, points to an alteration of about 4 per cent. of sucrose.

Six tins of another preparation which had been kept for a considerable time and which, on opening, exhibited varying signs of alteration, the milk being discoloured and thickened, were mixed and distributed to members of the Committee. The samples were analysed in the various laboratories by this method, with the following results:

TABLE VI

Laboratory	Original sucrose Per Cent.
A	42·80
B	42·94
C	42·68
D	42·90
E	42·63
F	42·99
G	42·73
Mean	42·81
Maximum deviation from the mean	0·18
Mean deviation from the mean	0·11

As mentioned at the beginning of this section, original sucrose can be determined by combination of polarimetric measurement of the inverted solution and the reducing action of the inverted solution towards copper solution or chloramine-T. The chloramine-T method is the one recommended, but by the use of copper solution satisfactory results have been obtained. The Lane and Eynon method[7] was used for determining the copper-reducing power, solutions containing lactose and invert sugar in approximately the proportions which would be obtained from a normal condensed milk in similar dilution being used as a control, thus giving a comparison for reference to Lane and Eynon's tables. It is not necessary to describe the method in detail, but the results obtained by it are included in Table VII with those obtained by the chloramine-T and Modified Barfoed methods. The analyses recorded in this table are those of old sweetened condensed milks, more or less altered during storage, and they afford confirmation of the view that dextrose, laevulose and laevan formation is the usual, and in the experience of the Committee the only, change which takes place in the sucrose. In these analyses the laevulose was determined in all cases by the Hinton and Macara process, and in the analyses with Modified Barfoed reagent the lactose figure is taken from the chloramine-T analyses.

TABLE VII

	Milk A		Milk B	
Method	Chloramine-T and polarisation after inversion Per Cent.	Modified Barfoed and polarisations before and after inversion Per Cent.	Chloramine-T and polarisation after inversion Per Cent.	Modified Barfoed and polarisations before and after inversion Per Cent.
Sucrose	33·09	33·68	30·83	29·41
Lactose (anhydrous)	14·39	14·39	14·94	14·94
Dextrose	5·50	4·67	7·15	7·21
Laevulose	1·45	1·45	1·72	1·72
Laevan	3·65	2·90	4·89	4·94
Direct				
$[\alpha]^{20}_D$ calculated ..	+29·60°	+29·93°	+28·38°	+27·44°
found ..	+29·75°	+29·75°	+27·21°	+27·21°
Original sucrose calculated from the above figures	43·54	42·55	44·42	43·11

	Milk C		Milk D	
Sucrose	33·29	33·25	35·40	35·95
Lactose (anhydrous)	11·21	11·21	11·44	11·44
Dextrose	4·33	4·03	2·75	2·09
Laevulose	1·66	1·66	1·86	1·86
Laevan	2·40	2·13	0·80	0·21
Direct				
$[\alpha]^{20}_D$ calculated ..	+27·79°	+27·74°	+29·11°	+29·41°
found ..	+27·63°	+27·63°	+29·26°	+29·26°
Original sucrose calculated from the above figures	41·51	40·91	40·63	39·92

	Milk E	
	Chloramine-T and polarisation after inversion Per Cent.	Copper reduction (Lane and Eynon) and polarisation after inversion Per Cent.
Sucrose	31·80	32·08
Lactose (anhydrous)	11·92	11·99
Dextrose	4·68	4·51
Laevulose	0·57	0·57
Laevan	3·70	3·55
Direct $[\alpha]^{20}_D$ calculated	+27·75°	+27·95°
found	+27·71°	+27·71°
Original sucrose calculated from the above figures	40·69	40·65

Method	Milk F Chloramine-T and polarisation after inversion Per Cent.	Milk F Lane and Eynon and polarisation after inversion Per Cent.	Milk F Modified Barfoed and polarisation before and after inversion Per Cent.
Sucrose	32·26	33·04	32·65
Lactose (anhydrous) ..	14·46	14·40	14·46
Dextrose	6·15	5·60	5·60
Laevulose	1·67	1·67	1·67
Laevan	4·03	3·54	3·54
Direct $[\alpha]_D^{20}$ calculated ..	+29·04°	+29·48°	+29·26°
found	+29·14°	+29·14°	+29·14°
Original sucrose calculated from the above figures ..	43·95	43·68	43·29

Milks A, B and F were of the same brand, and probably from the same batch. Milks C, D, and E were of another brand, and were probably of the same batch. E was analysed in January, 1931, C in September, 1931, D and A in December, 1931, B and F in January, 1932. It is interesting to note that a sample of the same make, and again probably of the same batch, as A and F, was analysed in September, 1929, before some of the processes used later had been devised; the analytical results obtained then have been recalculated, as far as possible, in the light of the more recent work, and are as follows:

	Per Cent.	
Sucrose	37·61	from chloramine-T and invert polarisation determinations.
Lactose (anhydrous) ..	15·02	Do.
Dextrose	3·18	
Laevulose	0·44	from Lane and Eynon method.
Laevan	2·47	
Direct $[\alpha]_D^{20}$ calculated ..	+33·25°	
found ..	+33·22°	
Original sucrose calculated from the above figures ..	43·66	

The analyses show that in September, 1929, about 6 per cent. of sucrose had broken down, and that the action continued (in the original sealed tins) until, by January, 1932, between 11 and 12 per cent. of sucrose had disappeared, with progressive formation of larger and larger quantities of dextrose, laevulose and laevan.

During the course of this work many sweetened condensed milks of commerce have been examined. It would seem that only when freshly prepared are these free from hydrolytic products of sucrose; amounts of these products corresponding with 0·2 to 0·5 per cent. of altered sucrose are common, although the milk is apparently quite sound.

(IX) DETERMINATION OF TOTAL MILK SOLIDS IN ALTERED SWEETENED CONDENSED MILK

It has been shown that after extensive alteration of the sucrose, the percentage of sucrose originally present can be determined. The total solids, however, will be determined with the altered sucrose present. In so far as sucrose is converted into invert sugar, the total solids will be higher than the original total solids, 1 part of sucrose giving 1·053 part of invert sugar. On the other hand, in so far as the laevulose is condensed to laevan, there is a loss of total solids, 1 part of laevulose giving 0·9 part of laevan. If all the laevulose is converted into laevan, the loss by condensation is equal to the gain by hydrolysis. In any of the cases investigated by the Committee there would have been, on balance, a slight increase of total solids, resulting in a slightly higher figure for total milk solids if these are obtained by subtraction of the "original sucrose" from total solids as determined. The error, giving a slight credit to total milk solids, may be neglected.

RECOMMENDATIONS

That for the purpose of the Public Health (Condensed Milk) Regulations (it being understood that the sample is a product prepared from milk and sucrose only):

I. Sweetened condensed milk should be examined by the Modified Barfoed process described in Appendix II to this report;

II. If no significant alteration is disclosed by this examination, the percentage of total milk solids should be determined by subtracting the percentage of sucrose determined by the method recommended in *Report No.* 2 from the percentage of total solids determined by the method described in *Report No.* 1;

III. If significant alteration is disclosed, the percentage of total milk solids should be determined by subtracting the percentage of original sucrose, determined as described in Appendix IV to this Report, from the percentage of total solids determined by the method described in *Report No.* 1.

APPENDIX I

PREPARATION OF SERUMS

PREPARATION OF SAMPLE.—Mix the sample as in the manner prescribed in *Report No.* 1[8].

ZINC ACETATE — POTASSIUM FERROCYANIDE SERUM*

REAGENTS.—*Zinc Acetate Solution.*—21·9 grms. of crystallised zinc acetate, $Zn(C_2H_3O_2)_2$, $2H_2O$, and 3 ml. of glacial acetic acid, in water, made up to 100 ml.

Potassium Ferrocyanide Solution.—10·6 grms. of crystallised potassium ferrocyanide in water made up to 100 ml.

Concentrated Ammonia Solution, nominal S.G. 0·880.

Dilute Ammonia Solution.—10 ml. of concentrated ammonia solution diluted with water to 100 ml.

Dilute Acetic Acid Solution approximately equivalent to the dilute ammonia solution.

PROCEDURE.—Transfer to a 100 ml. beaker an accurately weighed quantity, approximately 40 grms., of the well-mixed sample; add 50 ml. of hot distilled water (80°–90° C.); mix; transfer to a 200 ml. measuring flask, washing in with successive quantities of distilled water at 60° C., until the total volume is from 120 to 150 ml. Mix; cool to air temperature, and then add 5 ml. of the dilute ammonia solution. Again mix, and then allow to stand for 15 minutes. Add a sufficient quantity of the dilute acetic acid solution to neutralise the ammonia added (the exact equivalent is determined beforehand by titration), and again mix.

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* This is the same serum as is used for the determination of sucrose according to Report No. 2. The procedure for determining the specific rotation of the inverted serum (Appendix IV) is identical with that described in that Report.

Add, with gentle mixing, 12·5 ml. of zinc acetate solution and mix, followed in the same manner by 12·5 ml. of potassium ferrocyanide solution. Bring the contents of the flask to 20° C., and add distilled water (at 20° C.) up to the 200 ml. mark.

> Up to this stage all additions of water or reagents should be made in such a manner as to avoid formation of air bubbles, and, with the same object in view, all mixings should be made by rotation of the flask rather than by shaking. If bubbles are found to be present before completion of dilution to 200 ml., their removal can be assisted by temporary attachment of the flask to a vacuum pump, and rotation of the flask.

Close the flask with a dry stopper and mix thoroughly by shaking. Allow to stand for a few minutes, and then filter through a dry filter paper, rejecting the first 25 ml. of filtrate.

This serum is used for

(*a*) Modified Barfoed method. (Appendix II.)
(*b*) Determination of $[\alpha]_D^{20}$ of inverted solution. (Appendix IV.)
(*c*) If desired, for approximate chloramine-T titration. (Appendix IV.)
(*d*) Determination of laevulose. (Appendix III.)

PHOSPHOTUNGSTIC ACID SERUM

REAGENT.—*Phosphotungstic Acid Precipitant.* 50 grms. of crystalline sodium tungstate, $Na_2WO_4,2H_2O$, and 6 grms. of crystalline disodium phosphate are dissolved in about 200 ml. of distilled water, and 220 ml. of 2 *N* hydrochloric acid solution (or the equivalent amount of acid of other normality) are added slowly with stirring. The solution is diluted to 500 ml. and filtered. The acidity of the reagent should be so adjusted that 20 ml. require approximately 16·0 ml. of *N*/2 sodium hydroxide solution when titrated with methyl orange as indicator, and the p_H of the reagent, diluted to five times its volume with water, is approximately 1·3.

PROCEDURE.—Transfer to a 200 ml. measuring flask an accurately weighed quantity of 10 grms. of the well-mixed sample by successive quantities of distilled water at about 60° C., using about 120 ml. of water in all. Mix; cool to air temperature, and add, with gentle mixing, 10 ml. of the phosphotungstic acid reagent. Bring the contents of the flask to 20° C., and add distilled water (at 20° C.) up to the 200 ml. mark.

Up to this stage all additions of water or reagents should be made in such a manner as to avoid formation of air bubbles (see under zinc acetate and potassium ferrocyanide serum, above).

Close the flask with a dry stopper and mix thoroughly by shaking. Allow to stand for 10 minutes, and then filter through a dry filter paper, rejecting the first 25 ml. of filtrate.

(In the case of small samples the full quantity given above may not be available. If the prescribed quantity of 10 grms. is departed from, the amount of the phosphotungstic acid reagent must be varied so that its volume in ml. is numerically equal to the weight of sample taken in grms. The calculation in Appendix IV [ii] for the phosphotungstic acid serum holds only when this relationship is maintained and for a 5 per cent. serum.)

This serum is used for the chloramine-T titration.

APPENDIX II

MODIFIED BARFOED PROCESS

REAGENT.—*Copper Solution.*—Dissolve 60 grms. of crystallised sodium acetate in water, add 105 ml. of *N*/1 acetic acid and make up to 1 litre with water.

Transfer to a dry bottle; add 52 grms. (or more) of finely powdered crystallised copper acetate and shake to saturation. Filter.

Ferric Sulphate Solution.—Dissolve 50 grms. of ferric sulphate in about 400 ml. of water, to which 109 ml. of concentrated sulphuric acid has been added. Make up to 1 litre with water and filter. Before use this solution should be treated with *N*/10 permanganate until the colour of the latter ceases to be discharged.

N/10 Potassium Permanganate Solution.

PROCEDURE.—Introduce 25 ml. of serum (zinc serum: Appendix I) into a thin-walled boiling tube (internal measurements 8 × 1¼ inches); add 70 ml. of the copper solution; mix; cover the tubes with a watch-glass and immerse, to the level of the liquid in the tube, in the water in a large water-bath maintained at 80° C. for 20 minutes. Remove; cool in running water; filter on asbestos by suction and wash the tube and filter containing the cuprous oxide rapidly a few times with freshly boiled distilled water, rejecting the filtrate and washings. Dissolve the cuprous oxide (including any remaining in the tube) in 20 ml. of the ferric sulphate solution; wash the asbestos pad with cold freshly-boiled distilled water, adding the washings to the ferric sulphate filtrate, and titrate with *N*/10 permanganate to faint permanent pink.*

Note.—A convenient asbestos filter may be prepared by inserting a loosely fitting glass bead into the neck of a Allihn filter tube; above the bead is placed a layer of glass wool, and on this is laid the asbestos, which is added as a wet pulp and drawn on to the glass wool by suction. Solution of the cuprous oxide is rapidly effected by pipetting the ferric sulphate solution into the reduction tube, transferring to the Allihn tube and thoroughly mixing the surface asbestos layers with the sulphate solution by means of a flat-ended glass rod, leaving the lower asbestos layers and the glass wool undisturbed.

APPENDIX III

HINTON AND MACARA PROCESS FOR DETERMINATION OF LAEVULOSE[2]

REAGENTS.—*Sucrose Solution.*—Approximately 9 grms. per 100 ml. (freshly prepared).

Iodine Solution.—13 grms. of iodine and 15 grms. potassium iodide per 100 ml.

Mixed Alkali Solution.—Equal parts of 2 *N* sodium carbonate and 2 *N* sodium hydroxide.

Sulphuric Acid.—Approximately 5 *N*.

Sodium Sulphite Solution.—20 per cent. w/v.

Dilute Sodium Sulphite Solution.—2 per cent. freshly prepared; or diluted from the 20 per cent. solution.

Luff's Solution.—Dissolve 25 grms. of crystallised copper sulphate in 100 ml. of water; 50 grms. of citric acid in 50 ml. of water; 388 grms. of $Na_2CO_3, 10H_2O$ in 300 or 400 ml. of luke-warm water. Add the citric acid solution to the sodium carbonate solution, and then add the copper solution. Mix, cool, make up to 1 litre, and filter.

Note.—This solution should be accurately prepared, and 10 ml. of the finished solution should require approximately 45 ml. of *N*/2 sulphuric acid for neutralisation to methyl orange.

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* If the titration exceeds about 15 mls. *N*/10 $KMnO_4$ the test should be repeated with a suitable quantity of serum made up to 25 ml. For specially accurate work this dilution should be made with a serum prepared from fresh milk and sucrose.

Iodate-iodide Solution.—2·7 grms. of potassium iodate, 30 grms. of potassium iodide, and 10 ml. of $N/2$ sodium hydroxide solution per litre.

Potassium Oxalate Solution.—A saturated aqueous solution.

Sodium Thiosulphate Solution.—$N/20$.

Soluble Starch Solution.—Approximately 2 per cent.

Control Serum.—Prepared from fresh milk, using 100 ml. of milk with the same quantities of ammonia and acetic acid and precipitants as for 40 grms. of condensed milk, made up to 200 ml. and filtered.

PROCEDURE.—(i) *Oxidation of the Aldose Sugars.*—Pipette 10 ml. of the prepared condensed milk serum (zinc serum, Appendix I) and the same amount of the control serum into 250 ml. conical flasks, ensuring that the liquid does not flow on to the sides of the flasks. To the condensed milk serum add 10 ml. of water, and to the control serum 10 ml. of the sucrose solution.

Note.—Some workers find it preferable to add 2 ml. of a 0·5 per cent. solution of invert sugar to each serum so as to ensure a perceptible reduction in the control; this is termed "sensitising invert." Such addition makes no difference to the subsequent procedure.

To each, then add exactly 5 ml. of the iodine solution and exactly 6 ml. of the $2\,N$ mixed alkali solution; mix gently, and allow the flasks to stand for 10 minutes at from 18° C. to 20° C. Acidify with 1·6 ml. of $5\,N$ sulphuric acid, and remove the liberated iodine, first, with 20 per cent. sodium sulphite solution, and, finally, after adding 6 drops of soluble starch solution, with the 2 per cent. sulphite solution. (This operation should have the precision of a titration, though the quantities of sulphite solution needed are not measured; it should be conducted as rapidly as possible.) When all free iodine is eliminated, immediately add one drop of methyl orange solution and neutralise with the $2\,N$ mixed alkali solution.

Note.—The time elapsing between acidifying with $5\,N$ sulphuric acid and neutralising with the mixed alkali should not exceed 2 minutes, to avoid the danger of inversion of the sucrose.

(ii) *Treatment with Luff's Solution.*—To the contents of each flask add 20 ml. of Luff's solution; cover with a watch-glass and heat the contents to boiling on a plain wire gauze over a burner regulated so that boiling takes place in 2 minutes; impinging of the flame or hot gases on the sides of the flask should be prevented by an asbestos sheet with central hole of suitable dimensions placed in contact with the wire gauze. When boiling takes place, transfer the flask to an asbestos-covered gauze already heated by a small Bunsen flame, attaching a reflux condenser, and maintain gentle ebullition for exactly 10 minutes.

Remove from the flame and cool in running water for four or five minutes.

Titration of the Reduced Copper.—Add exactly 25 ml. of the iodate-iodide solution and 20 ml. of saturated potassium oxalate solution. Acidify carefully, while swirling, with 20 ml. of $5\,N$ sulphuric acid. Shake round (with some care, as frothing occurs) until the precipitate of cuprous oxide (which is partly converted into white cuprous iodide) has dissolved, and titrate with $N/20$ thiosulphate. No further addition of starch should be required. The end-point is distinguished by a sharp change to a fine light blue (the colour of the cupric salt).

Calculation of the Laevulose.—The difference between the titrations of the sample serum and the control serum, as ml. of $N/20$ thiosulphate solution, multiplied by 0·064, gives the percentage of laevulose in the sample, uncorrected for the volume of the clarification precipitate. (This factor is strictly correct only for a 20 per cent. serum, *i.e.* if exactly 40 grms. of condensed milk was diluted to 200 ml. in the preparation of the serum.) The correction for volume of precipitate, if required, is calculated as in Appendix IV, i.

APPENDIX IV

THE DETERMINATION OF "ORIGINAL SUCROSE"

(i) SPECIFIC ROTATION OF THE INVERTED SERUM

REAGENT.—*Hydrochloric Acid Solution* = 6·34 times normal.

INVERSION.—Pipette into a 50-ml. measuring flask 40 ml. of the filtrate obtained by zinc clarification (see Appendix I); add 6 ml. of 6·34 *N* hydrochloric acid. Immerse the entire bulb of the flask for 12 minutes in a water-bath maintained at 60° C., mixing by rotatory movement during the first three minutes, in which time the contents of the flask should have attained the temperature of the bath. Cool, and make up to the 50 ml. mark at 20° C., with distilled water; mix, and allow to stand for one hour.

INVERT POLARISATION.—Determine the rotation at 20° C.

CALCULATION.

W = weight of sample taken in grms.
F = percentage of fat in the sample,
P = „ „ protein (N × 6·38) in the sample,
V = volume (in ml.) to which the sample is diluted before filtration,
v = correction in ml. for volume of precipitate produced during clarification,
I = observed invert polarimeter reading,
l = length in dm. of polarimeter tube,
*R = specific rotation of the inverted serum ($[\alpha]_D^{20}$),

* *Note.*—If the mercury green line is used instead of the D line, the reading should be multiplied by 0·847 to convert to rotation for the D line.

then $$v = \frac{W}{100}\left[(F \times 1{\cdot}08) + (P \times 1{\cdot}55)\right],$$

and $$R = \left(\tfrac{5}{4} \times I\right) \times \frac{V-v}{V} \times \frac{V}{l \times W}$$

(ii) THE CHLORAMINE-T TITRATION

REAGENTS.—*N/20 Chloramine-T Solution.*—Containing 7·04 grms. per litre, freshly prepared, and protected from light.

Standard Sodium Thiosulphate Solution.—Preferably rather stronger than *N*/20, so that 50 ml. of the chloramine-T solution can be titrated without refilling a 50 ml. burette.

Note.—The thiosulphate must be accurately standardised against pure potassium dichromate by the method of Popoff and Whitman.[9] The procedure is as follows:

To 25 ml. of *N*/10 potassium dichromate solution add 20 ml. of 10 per cent. potassium iodide solution and 10 ml. of 2 *N* hydrochloric acid; stopper the flask, and allow to stand in the dark for 10 minutes; then titrate with the thiosulphate.

N/2 Sodium Hydroxide Solution.

N/10 Sodium Hydroxide Solution.

Soluble Starch Solution.—Approximately 2 per cent.

PROCEDURE.—*Inversion.*—Pipette 25 ml. of the phosphotungstic acid serum (see Appendix I) into a 100-ml. measuring flask, add 15 ml. of distilled water and 5 ml. of 6·34 *N* hydrochloric acid. Immerse for 12 minutes the entire bulb of the flask in a water-bath maintained at 60° C., mixing by rotatory movement during the first 3 minutes, in which time the contents of the flask should have attained the temperature of the bath. Cool, add *N*/2 sodium hydroxide solution, continually mixing, until neutral, carrying the addition of alkali to the point of a definite turbidity (no internal indicator should be used). Cool and make up to the 100 ml. mark at 20° C. with distilled water.

Titration of inverted and neutralised Serum.—Into one of two 250 ml. flasks or bottles pipette 25 ml. of the inverted neutralised serum which has been diluted to 100 ml.; into the other pipette 25 ml. of water (as a blank). To each add 3 ml. of *N*/10 caustic soda solution, followed by 20 ml. of 10 per cent. potassium iodide solution, then, into each, pipette accurately 50 ml. of the *N*/20 chloramine-T solution; close the flasks or bottles and leave in the dark for 1½ hours at a temperature of from 17° to 18° C. At the end of this time add to each flask 10 ml. of 2 *N* hydrochloric acid and titrate at once with the thiosulphate solution, with starch solution as indicator.

Note.—All measuring flasks, pipettes and burettes must be accurately calibrated, special attention being paid to drainage of the burette, which should be calibrated in the manner in which it is used for the titration. Readings of the burette are made to 0·01 ml.

CALCULATION.

S = percentage of "original sucrose" in the sample,
E = iodine absorbed per 100 grms. of sample,
W = weight of sample taken in grms.,
F = percentage of fat in the sample,
P = percentage of protein (N × 6·38) in the sample,
V = volume (in ml.) to which the sample is diluted before filtration,
v = correction in ml. for volume of precipitate produced during clarification,
n = difference between the inverted serum and the blank titrations in ml. *N*/20 thiosulphate solution.

Then, for calculation of the original sucrose,

$$v = \frac{W}{100}[(F \times 1{\cdot}08) + (P \times 0{\cdot}74) + 3{\cdot}75] \text{ ml.}$$

$$E = (n - 0{\cdot}15^*) \times 63{\cdot}46 \times 0{\cdot}032 \times \frac{V-v}{V}$$

and $$S = 0{\cdot}964\, E - 1{\cdot}29\, R.$$

Addendum.—If it is desired to determine the chloramine-T figure on the zinc serum, the procedure is as follows:—Pipette 20 ml. of the inverted serum (which has been used for the determination of $[\alpha]_D^{20}$ invert) into a 250-ml. flask, add *N*/2 sodium hydroxide solution, with continual mixing (approximately 31 ml. will be required) until neutral, neutrality being shown by a distinct permanent turbidity.

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* This is the correction for absorption by non-sugars, and applies only to the quantities prescribed and for a usual proportion of non-fatty solids in the milk.

Make up to the 250-ml. mark at 20° C. with distilled water and mix. 25 ml. of this solution are taken for the chloramine-T titration.

$$\text{Then} \qquad E = (n - 0{\cdot}15) \times \frac{63{\cdot}46}{32} \times \frac{V - v}{V}$$

$$\text{and, as before,} \qquad S = 0{\cdot}964\,E - 1{\cdot}29\,R.$$

(These formulae for the zinc serum apply strictly only to a 20 per cent. serum, *i.e.* if exactly 40 grms. of condensed milk was diluted to 200 ml. in the preparation of the serum.) As explained in the body of the Report, results obtained on the zinc serum are approximate only, and slightly low.

Note.—The volume of precipitate corrections are based upon the data recorded in *Report No.* 2 (THE DETERMINATION OF SUCROSE IN SWEETENED CONDENSED MILK).

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For and on behalf of the Sub-Committee,

(*Signed*) E. HINKS (*Chairman*),
E. B. HUGHES (*Hon. Secretary*)

July, 1932

Erratum.—*Report No.* 2, p. 2, line 33 (ANALYST, 1930, **55**, 112, line 33), *for* "sufficiently" *read* "not sufficiently."

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF SALFORD

REPORT OF THE CITY ANALYST FOR THE YEAR 1931

THE 1445 samples of food and drugs examined comprise 574 formal and 871 informal samples (47 adulterated).

BOTTLED MILK.—A type of cap which is very common in U.S.A. covers the whole of the top of the bottle, and is secured beneath the welted rim of the neck. It is to be regretted that this form (which prevents contamination of the rim) is not in use in this country.

The advent of bottled milk has presented a new difficulty in dealing with adulterated samples. Very few retailers have warranties from wholesalers for the quality of the milk they get from them, the argument being that it is not fair that the wholesaler should be held responsible for milk which has passed out of his hands. The crux of the matter is the question of "control," and, as the Salford Stipendiary observed during the hearing of a recent case, milk in bottles may well be held to be under the control of the bottlers until the seal is removed.

It was suggested to the local Milk Dealers' Association that bottlers of milk should adopt a form of warranty to be printed on the cap in some such terms as the following:—"The milk in this bottle is warranted pure and to contain all its natural fat and milk solids, by . . . (name and address of bottler)," and that the retailer should be given a written continuing warranty. The Association was not prepared to adopt this suggestion, although one large wholesaler has done so. During the past two or three years there have been several cases in which bottled milk sold by a retailer has been found to be below standard, and in which enquiry has proved that the retailer could not be held responsible for the deficiency. In future, deficiencies in bottled milk cannot be passed over, and retailers would be well advised to obtain warranties from the bottlers of the milk they sell.

FREEZING POINT OF MILK.—The extreme range in the freezing points of 257 samples of genuine milk, determined by means of the Hortvet apparatus, was —0·535° to —0·572° C., with an average of —0·551° C. One sample froze between —0·566° and —0·570° C. and one between —0·571° and —0·575° C.

"MARGARINE BLENDED WITH BUTTER."—An informal sample, labelled "Margarine blended with Butter," contained about 3·5 per cent. of butter, and a formal sample contained 5 per cent. of butter. In view of the decision in the case of *Anness* v. *Grivell* (in which the vendor sold a substance containing 4·5 per cent. of butter as "a very good mixture of margarine and butter"), it was considered that a prosecution would have little chance of success. It was not pointed out to the judges, however, in the case of *Anness* v. *Grivell*, that, although the Food and Drugs Act prohibits the sale of mixtures containing more than 10 per cent. of butter, the proviso applies to margarine, and the Act expressly provides that any mixture of butter and margarine must be sold simply as "margarine."

"HOUSEHOLD TURPENTINE."—Of 16 samples of turpentine examined, 8 were found to be adulterated with "white spirit," in amounts varying from 30 to 100 per cent. In several of these cases the article was described as "household turpentine," and was labelled "Not to be used for medicinal purposes." This raised a difficulty in instituting proceedings under the Food and Drugs Act, as the defence would have been that the sample could not be called a "drug" within the meaning of the Act. Proceedings were, therefore, taken under the Merchandise Marks Act, both the packers and the sellers being summoned. A conviction was secured, and each was fined £15, with £5 5s. costs.

H. E. MONK

Straits Settlements

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1931

IN his Annual Report the Government Analyst (Mr. J. C. Cowap) points out that the greater portion of the routine work is provided by the Monopolies Department, and is concerned with the protection of revenue. It consists in the examination of opium, chandu, imported or locally distilled liquors, toddy and deleterious drugs.

LIQUORS REVENUE ORDINANCE.—Of the 68 samples of brandy analysed for classification under the Liquors Revenue Ordinance, 1927,* 43 were passed as brandy; the remaining 25 were either refused admittance as brandy or the importers were asked to produce evidence that the liquor actually was brandy. In no case was such evidence produced.

Definition of Brandy.—Brandy is defined as a potable spirit manufactured from fermented grape juice and from no other materials. Brandy containing less than 60 grms. of esters in 100 litres of absolute alcohol is deemed to be adulterated unless satisfactory evidence is forthcoming from the place of origin that it is genuine. In the case of French brandies, practically the only ones imported, the "acquit blanc," or "acquit jaune d'or," issued by the French Government, is alone accepted. (Note: "Arrack" is ordinary rectified spirit; practically the whole of that imported is distilled in Java from sugar waste.)

DELETERIOUS DRUGS.—Thirty-six exhibits consisted chiefly of medicines for the cure of various diseases, including opium smoking. Many of them contained opium. One seizure of 9 bottles, labelled morphine hydrochloride, contained boric acid with a layer of quinine hydrochloride at the top of each bottle.

MEDICAL DEPARTMENT.—Samples examined for this department included water and sewage, poisons and toxicological exhibits, milk and other foods and drugs.

Tuba Root.—Among the poisons detected was tuba (or derris) root, a well-known Malay fish poison. The root is bruised in water with lime, and the milky emulsion is thrown into a stream to stupefy the fish. When used in sufficient quantity the emulsion can cause death in human beings. The root contains about 25 per cent. of resin soluble in acetone and alcohol, and this (and also the aqueous extract) is exported as an insecticide in increasing quantities from Singapore to Europe and U.S.A. The action of the resin on small fish is characteristic.

Milk.—The standards are 3·25 per cent. of fat and 8·5 per cent. of solids-not-fat.

POLICE DEPARTMENT.—Toxicological exhibits, counterfeit coins, fireworks and explosives were examined for this department.

Counterfeit Coins.—The total number of coins examined in 28 cases was 14,600. The hands and clothing of coiners frequently show traces of silver nitrate and nitric acid. These are recognised by the ordinary tests, *e.g.* mercuric chloride or potassium cyanide for silver stains. As the coins are trimmed with a small file, filings of metal are often found under the finger nails of coiners. These are scraped out and examined under the microscope. The metal is then dissolved in acid while still on the microscope slide, and the solution is touched with drops of appropriate reagents, *e.g.* mercuric chloride for tin. In several cases evidence was thus obtained.

IDENTIFICATION OF STARCH PASTE.—A starch of unusual type (East Indian arrowroot) used for pasting up seditious leaflets, was found to be identical with that in certain stains on the hands of a suspect. This starch, in spite of its name, is not in general commercial use, and is usually obtainable only from European shops; it is never used for bill posting. Unfortunately for himself, the accused mixed the starch with cold water, so that the granules on his poster and on his hands were easily recognised.

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* According to the Straits Settlements Liquors Revenue Ordinance, 1927, the following duties (*inter alia*) are imposed:—Arrack, brandy, $14.00 per proof gall.; brandy imported in bottle and not exceeding 81 per cent. of proof spirit, $10.50; brandy consigned from Great Britain or the British Dominions, $9.50; whiskey, rum and gin, $13.00; Japanese saki and Chinese samsu, $12.00; bitters and liqueurs not exceeding 100 per cent. of proof spirit, $13.00; sparkling wines, $6.00; do. from Great Britain or the British Dominions, $5.50; still wines (including medicated wines) exceeding 26 per cent. but not exceeding 42 per cent. of proof spirit, $4.50; do. from Great Britain or the Dominions, $4.20; still wine not exceeding 26 per cent. of proof spirit, $1.50; do. from Great Britain and the Dominions, $1.30; ale, beer, stout, porter, cider, and perry, $1.30; do. from Great Britain or the Dominions, $1.20 per gallon.

The preferential rates specified will not be applicable unless 25 per cent. of the brandy, wine, ale, etc., is the result of labour within the United Kingdom of Great Britain and Northern Ireland, the British Dominions within the meaning of the Statute of Westminster, 1931, or any Malay State under British Protection.

FACE POWDERS CONTAINING LEAD.—The discovery of lead in face powders, mentioned in the 1930 Report (ANALYST, 1931, **56**, 812), has led to the prohibition of the sale of such powders. Of 8 samples of Chinese origin examined in Penang Municipality, 2 contained an appreciable quantity of lead carbonate.

DOPING OF RACE-HORSES.—A number of samples of sweat and saliva of race-horses were examined for alkaloids in general, and caffeine and strychnine in particular, by the methods described by Lander (ANALYST, 1930, **55**, 474). It has never been suggested that horses in Singapore are doped to make them lose a race, but only to assist them to win.

Fertilisers and Feeding Stuffs Act, 1926

REVISION OF REGULATIONS

STATUTORY RULES AND ORDERS, 1932, No. 658*

THE Ministry of Agriculture and Fisheries and the Department of Agriculture for Scotland announce that, in pursuance of the powers conferred on them by Section 23 of the Fertilisers and Feeding Stuffs Act, 1926, they have made new Regulations entitled "The Fertilisers and Feeding Stuffs Regulations, 1932 (Statutory Rules and Orders, 1932, No. 658), to replace the Fertilisers and Feeding Stuffs Regulations, 1928." The new Regulations will come into operation on September 1st, 1932.

The principal matters in the Regulations affected by the revision may be grouped, for convenience, under two heads:—(*a*) the methods of sampling and analysis, and (*b*) alterations to the Schedules to the Fertilisers and Feeding Stuffs Act, 1926.

As regards (*a*), the provisions relating to the manner of taking samples have been rearranged and amended in certain respects, mainly in order to facilitate the work of the officials concerned. The methods of analysis have been amended by the adoption of the British Standard Test Sieve, Mesh No. 100, in place of the present prescribed sieve, for the determination of the fineness of grinding of basic slag, etc.; and also by the inclusion of a method of analysis for the determination of citric-soluble phosphoric acid.

As regards (*b*), the fresh amendments are confined to the First, Second and Fourth of the Schedules to the Act.

It may be explained that the First and Second of the Schedules to the Act include the classes of articles in respect of which the seller is required under the Act to give to the purchaser a statutory statement, which has effect as a warranty, containing certain prescribed particulars. In the Fourth Schedule to the Act the names of the more commonly used fertilisers and feeding stuffs are defined, and the use in a statutory statement of any of these names constitutes a warranty that the article accords with the relative definition.

With one exception, the present amendments to these Schedules relate to feeding stuffs, the exception being "Lime mixtures," which, under the New Regulations, is now included amongst the fertilisers in the Second Schedule.

Alfalfa meal has been added to the Second Schedule, and has been defined in the Fourth Schedule as "Alfalfa (Lucerne) as grown, dried and ground, to which no other matter has been added."

The entry "Barley Meal" in both the First and Fourth Schedules is now replaced, in the New Regulations, by two entries, namely, "Barley Meal" and "Barley Meal Grade II." These names are defined for the purpose of the Fourth Schedule, as follows:—

Barley Meal.—The meal obtained by grinding barley, as grown, which shall be the whole grain together with only such other substances as may reasonably be expected to have become associated with the grain in the field; the meal to contain not less than 96 per cent. of pure barley.

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* Copies of the new Regulations can be obtained from H.M. Stationery Office, Adastral House, Kingsway, W.C.2, and branches. Price 10d. exclusive of postage.

Barley Meal (Grade II).—The meal, other than barley meal, as defined above, obtained by grinding barley, as grown, which shall be the whole grain together with only such other substances as may reasonably be expected to have become associated with the grain in the field; the meal to contain not less than 90 per cent. of pure barley.

The definitions, in the Fourth Schedule, of Bean Meal and Pea Meal have been amended to read as follows:—

Bean Meal.—The meal obtained by grinding commercially pure beans of the species (1) *Vicia faba* (synonym, *Faba vulgaris*), or any of its varieties, commonly known as "horse bean," "field bean," or "broad bean"; or (2) *Phaseolus vulgaris*, the "true haricot bean," or any of its varieties, white or coloured.

Pea Meal.—The meal obtained by grinding commercially pure peas, as grown, of varieties of *Pisum sativum* or *Pisum arvense*.

The entries in the Schedules relating to Feeding meat and bone products have been varied, the chief point, perhaps, being that the definitions of Feeding meat meal and Feeding meat and bone meal in the Fourth Schedule have been amended with the object of fixing minimum percentages of albuminoids (protein) in these articles. The new definitions read as follows:

Feeding Meat Meal.—"The product, containing not less than 55 per cent. of albuminoids (protein) and not more than 4 per cent. of salt, obtained by drying and grinding animal carcases or portions thereof (excluding hoof and horn), to which no other matter has been added."

Feeding Meat and Bone Meal.—"The product, containing not less than 40 per cent. of albuminoids (protein) and not more than 4 per cent. of salt, obtained by drying and grinding animal carcases or portions thereof (excluding hoof and horn) and bone, to which no other matter has been added."

MINISTRY OF AGRICULTURE AND FISHERIES,
10, WHITEHALL PLACE, LONDON, S.W.1,
29th June, 1932

United States Department of Agriculture

FOOD AND DRUG ADMINISTRATION*

NEW AND REVISED DEFINITIONS AND STANDARDS FOR FOOD PRODUCTS

MAYONNAISE, mayonnaise dressing, mayonnaise salad dressing, is the semi-solid emulsion of edible vegetable oil, egg yolk, or whole egg, a vinegar, and/or lemon juice, with one or more of the following: Salt, other seasoning commonly used in its preparation, sugar and/or dextrose. The finished product contains not less than 50 per cent. of edible vegetable oil.

Milk bread is the product, in the form of loaves or smaller units, obtained by baking a leavened and kneaded mixture of flour, salt, yeast, and milk or its equivalent (milk solids and water in the proportions normal to milk); with or without edible fat or oil, sugar and/or other fermentable carbohydrate substance. It may also contain diastatic and/or proteolytic ferments, and such minute amounts of unobjectionable salts as serve solely as yeast nutrients.† The flour ingredient may include not more than 3 per cent. of other edible farinaceous substance. Milk bread contains, one hour or more after baking, not more than 38 per cent. of moisture.

The definition for rye bread has been deleted.

Farina macaroni, farina spaghetti, farina vermicelli, are plain alimentary pastes in the preparation of which farina is the only farinaceous ingredient used and are distinguished by their characteristic shapes.

Ginger ale is the carbonated beverage prepared from ginger ale flavour, harmless organic acid, potable water, and a syrup of one or more of the following: Sugar, invert sugar, dextrose, with or without the addition of caramel colour.

Ginger ale flavour, ginger ale concentrate, is the beverage flavour in which ginger is the essential constituent, with or without aromatic and pungent ingredients, citrus oils, fruit juices, and caramel colour.

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* *Service and Regulatory Announcements, Food and Drug No.* 2 (Second Revision), Supplement No. 1.

† The propriety of the use of minute quantities of oxidising agents as enzyme activators is reserved for future consideration and without prejudice.

Sarsaparilla is the carbonated beverage prepared from sarsaparilla flavour, potable water and a syrup of one or more of the following: Sugar, invert sugar, dextrose; with or without harmless organic acid, and with or without the addition of caramel colour.

Sarsaparilla flavour is the beverage flavour prepared from oil of sassafras and methyl salicylate (or oil of wintergreen or oil of sweet birch) with or without other aromatic and flavouring substances and caramel colour. It derives its characteristic flavour from oil of sassafras and methyl salicylate.

Root beer is the carbonated beverage prepared from root beer flavour, potable water, and a syrup of one or more of the following: Sugar, invert sugar, dextrose; with or without harmless organic acid, and with or without the addition of caramel colour.

Root beer flavour, root beer concentrate, is the beverage flavour in which oil of sassafras and methyl salicylate (or oil of wintergreen or oil of sweet birch) are the principal flavouring constituents, and contains other flavouring substances, with or without the addition of caramel colour.

Birch beer is the carbonated beverage prepared from birch beer flavour, potable water, and a syrup of one or more of the following: Sugar, invert sugar, dextrose; with or without harmless organic acid, and with or without the addition of caramel colour.

Birch beer flavour, birch beer concentrate, is the beverage flavour in which methyl salicylate (or oil of sweet birch or oil of wintergreen) and oil of sassafras are the principal flavouring constituents, with or without other flavouring substances, and with or without caramel colour. The flavour of methyl salicylate predominates.

Cream soda water, "cream soda," is the carbonated beverage prepared from cream soda water flavour, potable water, and a syrup of one or more of the following: Sugar, invert sugar, dextrose; with or without harmless organic acid, and with or without the addition of caramel colour.

Cream soda water flavour, cream soda water concentrate, is the beverage flavour prepared from vanilla, tonka, vanillin, or coumarin, singly or in combination, together with other flavouring substances; with or without the addition of caramel colour.

Issued December, 1931

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Detection of Washed, Abraded, and Oiled Eggs. P. F. Sharp. (*Ind. Eng. Chem.*, 1932, **24**, 941-946.)—If dirty eggs which have or have not been cleaned are sold, they may go into immediate consumption before any bacteria present cause marked spoilage. If, however, such eggs are kept either at a comparatively high temperature or for an appreciable time, bacterial deterioration may occur in from 3 to 50 (or even more) per cent. of them, according to the amount of the dirt on the shell and to the treatment they have undergone. Of eggs which have never been dirty and have been properly kept, only 2 or 3 per cent. will show bacterial development.

Attempts to recognise washed eggs by testing for the removal of protein from the shell proved unsuccessful, but micro-precipitation tests of an extract of the shell for potassium and chlorides gave positive results with unwashed, and negative results with washed, eggs. A drop of water was placed on the clean upper surface of the shell and left for 5 minutes, after which it was removed from the inverted egg to a microscope slide, to be tested for either chloride or potassium. With an unwashed egg, addition of a drop of 0·1 N silver nitrate solution to the water drop yields a precipitate, usually corresponding in amount with that obtained with one drop of 0·005 *N* sodium chloride solution. The precipitate varies in appearance with different eggs, and is best viewed under strong lateral illumination and with a magnification of twenty to forty diameters. For the potassium test, the following reagent is used: 20 grms. of cobaltous nitrite, $Co(NO_2)_2, 6H_2O$, 25 grms. of sodium nitrite, 65 c.c. of distilled water, and 10 c.c. of glacial acetic acid are mixed, heated to boiling after violent evolution of fumes ceases, left to cool for 24 hours, made up to 150 c.c., and filtered. When a drop of this solution is mixed, by means of a fairly stiff wire, with the drop on the slide, crystallisation of the potassium cobaltinitrite occurs usually within five minutes, but sometimes only after about 15 or 20 minutes. In over 1100 cases, the test for chloride gave erroneous results in about a dozen instances, while the potassium test failed or gave uncertain indications with two only out of over 500 eggs.

Eggs washed with egg albumen solution are recognisable by the heavy precipitate given by the shell extract with Millon's solution, and those washed with soap solution by their feel. Treatment of eggs with oil to retard evaporation and escape of carbon dioxide does not interfere with the tests for potassium and chloride. The greatest interference with this test for washed eggs occurs with storage eggs. During the storage the potassium chloride largely disappears from the surface of the shell; the time required for the disappearance of this salt diminishes as the degree of humidity of the store increases, but probably lies between 4 and 8 months for eggs kept at 0° C. and under conditions otherwise normal. Usually the potassium chloride has not entirely vanished, and tests made show that an experienced operator can nearly always distinguish between washed, unwashed, and storage eggs in uniformly-treated lots.

If the dirty spots on eggs have been cleaned by scraping with emery paper, sand paper, steel wool, etc., the protein and the potassium chloride are removed from the scraped regions. If a sand-blast has been used, the eggs generally yield an extract which gives no test for potassium or chloride. When, however, an abraded egg is immersed in the solution of a dye, such as methylene blue, malachite green, safranine, etc., capable of staining the protein material on the surface of the shell, the scraped parts, being unstained, show up quite clearly. The eggs, in a metal tray or basket, are immersed, first in water for 4 or 5 seconds (to prevent the dye from penetrating too deeply), and then in a solution of 1 grm. of rosaniline hydrochloride per litre for 30 seconds. After observation, the eggs are placed for about 1 minute in a 2 per cent. solution of sodium bisulphite to reduce the dye, and are afterwards washed in water; they are then in saleable condition.

Treatment of eggs with a sand-blast, either to remove dirt or to "deprocess" eggs which have been oiled, cannot be detected under the microscope, the scarifying effect being less than might be expected. Oil-treated eggs can usually be recognised by the appearance of the shell, especially if a whole case is examined, but it is sometimes difficult to ascertain in this way if individual eggs have been oiled. Such eggs can, however, be detected by dipping the end of the egg into ether for a second; in a good light an oily ring can then be seen at the edge of the ether-treated part. Removal of the oily appearance of the eggs by sand-blasting is often practised, but eggs thus treated still show the oily ring left by the ether.

T. H. P.

Determination of Total Solid Matter and Density of Egg White by means of the Refractometer. H. J. Almquist, F. W. Lorenz and B. R. Burmester. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 305–306.)—Since egg white may be considered as protein, mineral matter and water only, and the mineral part is a small and usually constant fraction of the total, the system behaves as a binary mixture, and either the index of refraction or the specific gravity, but more conveniently the former, may be measured in order to find the total solids. The graphs may be constructed from the following points taken accurately from the plotted curves:

Refractive index $n_D^{25°}$	Total solids Per Cent.	Specific gravity at 25°/25° C.
1·3520	10·55	1·0312
1·3600	14·55	1·0442

The method cannot be used for egg yolk or whole egg, since these mixtures contain more than two major components. D. G. H.

Rye Germ Oil. A. W. Stout and H. A. Schuette. (*J. Amer. Chem. Soc.*, 1932, **54**, 3298–3302.)—The rye germ oil was obtained by extracting rye embryo (containing 11 per cent. of oil) with sulphur-free petroleum spirit. The embryo was obtained by repeated sifting and air-cleaning of so-called rye germ stock, a milling bye-product. The oil was of a deep golden-brown colour, and semi-drying, plastic at —60° C. It has the following characteristics: Sp.gr., at 20°/20° C., 0·9229; $n_D^{20°}$, 1·4779; saponification value, 176·8; iodine value (Wijs), 139·9; Reichert–Meissl value, 0·05; Polenske value, 0·3; free fatty acids (as oleic), 2·9 per cent.; unsaponifiable matter, 7·28 per cent.; acetyl value, 20·19; soluble acids (as butyric), trace; insoluble acids (Hehner value), 84·45; iodine value of insoluble fatty acids, 133·57; and thiocyanogen value, 85·05; unsaturated acids, corrected, 77·46 per cent. (with iodine value 158·9, and saponification value 172·6); saturated fatty acids (corrected), 10·12 per cent. The unsaturated acids were separated in form of bromine addition compounds, and the saturated acids by separation of the methyl esters. The percentage composition of the oil was calculated to be: myristin, 2·33; palmitin, 8·11; stearin, 0·18; olein, 31·92; linolin, 44·05; linolenin, 4·99; unsaponifiable matter, 7·28; and undetermined, 1·14. The lecithin equivalent of a hypothetical di-oleyl derivative ($C_{44}H_{86}O_9NP$), was calculated from the phosphorus-content of the oil and its unsaponifiable matter, and was 1·33 per cent. for the former and 3·05 for the latter. A pronounced blue coloration is formed on addition of antimony chloride to the oil, and a still more pronounced coloration if the extracted unsaponifiable matter is used. (*Cf.* Croxford, ANALYST, 1930, **55**, 735.) D. G. H.

Quince Seed Mucilage. A. G. Renfrew and L. H. Cretcher. (*J. Biol. Chem.*, 1932, **97**, 503–510.)—The quince seed gum was prepared by extraction of the seeds with alcohol and ether, followed by separation of the mucilage with water, and precipitation with alcohol. A neutral gum soluble in water and containing 6 per cent. of ash resulted. By precipitation in slightly acid solution, faintly acidic gum insoluble in water and with less ash was obtained; this contained: uronic acid, 27·8; pentose, 33·0; ash, 2·0; and cellulose, 33·0 per cent. When hydrolysed with 0·5 N sulphuric acid, this gum yielded arabinose, a mixture of methylated and unmethylated aldobrionic acids and a cellulosic fraction. After further hydrolysis of 14 grms. of the calcium salts of the aldobrionic acids for 20 hours with 600 c.c. of 0·96 N sulphuric acid, 21 per cent. of the uronic acid had been destroyed. Calcium sulphate was removed, the concentrated solution was treated with 2 and with 6 volumes of alcohol, and about 2·3 grms. of unhydrolysed aldobrionic acid were recovered. The supernatant liquors were concentrated to dryness, and crystalline xylose was isolated from the portion soluble in alcohol. An 8 per cent. solution of this had a specific rotation of 19·1° after 2 hours, and this remained constant for 24 hours. D. G. H.

Composition of Iraq Dates. M. M. Cleveland and C. R. Fellers. (*Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 267–268.)—The edible portion of two samples of Iraq dates had the following percentage composition:

	Moisture	Ash	Protein	Fat (ethereal extract)	Reducing sugars (as invert sugar)	Total carbohydrates (other than crude fibre)	Crude fibre	Sucrose
Hallowi	19·0	2·22	1·72	1·90	73·50	73·67	2·17	None
Sayer	18·0	1·59	2·16	0·31	—	76·14	1·90	—

The percentage composition of the ash was as follows:

	Potassium oxide	Sodium oxide	Calcium oxide			anhy	Alum	Copp	Chlo	Sulp anhy	M	
Hallowi	42·7	2·47	4·51	5·86	0·26	9·50	0·48	0·015	13·33	6·44	0·21	7·24
Sayer	40·8	2·65	6·96	6·77	0·23	7·47	—	0·014	16·64	7·62	0·30	—

The alkalinity of the ash (in terms of c.c. of N hydrochloric acid) was 16·7 and 15·9. D. G. H.

Identification of White Wine made from Red Grapes. G. Graff. (*Chem.-Ztg.*, 1932, **56**, 704.)—White wine prepared by decolorising red wine with charcoal gives a fairly stable pink coloration when 10 c.c. of the sample are treated with 3 to 5 drops of 10 per cent. hydrochloric or sulphuric acid, unless a very large excess of the decolorising charcoal has been used, which is exceptional. In any case, a pink coloration in this test indicates that the wine was made wholly or in part from red grapes expressed while still white, or from bleached red wine.

Changes in Fats during Frying. F. R. Porter, H. Michaelis and F. G. Shay. (*Ind. Eng. Chem.*, 1932, 24, 811–813.)—When animal fat, vegetable oil, or hydrogenated vegetable oil is heated at 176° to 232° C., there is a slight formation of fatty acid, an increase in viscosity, particularly at the higher temperature, and some formation of gummy substances, probably due to polymerisation. If water is present, the breaking-down of the fat, with the production of acidity, is a direct result of the action of the water. At first the action is slow, but when about 0·75 per cent. of acid (calculated as oleic acid) has been produced, it proceeds more rapidly. The percentage quantity of free fatty acid in a used fat is a fairly reliable measure of the objectionable property of the fat of imparting an unpleasant flavour to food fried therein; this unpleasant flavour appears when the fat contains about 2 per cent. of free fatty acids. W. P. S.

Iodine Value and Refractive Index of Perilla Oil. C. A. Lathrap. (*Ind. Eng. Chem.*, 1932, 24, 826–827.)—Six samples of perilla oil, cold-pressed from hand-picked seeds, had iodine values (Wijs) from 192·0 to 208·6, and refractive indices (n^{25}_{D}) from 1·4800 to 1·4820. One hundred samples of imported perilla oil, considered to be genuine, had iodine values ranging from 193·3 to 207·0, and refractive indices from 1·4802 to 1·4818. In the case of twenty of these oils, the refractive index was higher than 1·4815. W. P. S.

The Component Glycerides of Partially Hydrogenated Fats. T. P. Hilditch and E. C. Jones. (*J. Chem. Soc.*, 1932, 805–820.)—Olive oil was chosen for investigation on account of its comparatively simple structure and the fact that it contains a large amount (at least 60 per cent.) of tri-unsaturated glycerides, and cottonseed oil because of its content of saturated acids (over 20 per cent., almost all of which is palmitic). The experimental results of the investigation, which are collected in two tables, show the iodine values, the component fatty acids present in the whole fat (either calculated from observed fall in iodine value in conjunction with the analysis of the mixed fatty acids of the original oils, or found), the percentage of fully saturated glycerides, and the component fatty acids present in the latter. The figures are given as percentages by weight as determined and as molar percentages, owing to the varying molecular size of the component acyl radicals. The limits within which the molar percentages of the three classes of glycerides containing unsaturated radicals may vary are also given for each hydrogenated fat. The sequence of action involved in the conversion of a molecule of triolein into tristearin, and the experimental results (discussed in detail) lead to the conclusion that only one olein group undergoes hydrogenation at each effective contact with the catalyst, the semi-hydrogenated glyceride then leaving the catalyst and requiring fresh adsorption before further addition of hydrogen occurs. Also, hydrogenation of the different classes of unsaturated glycerides is definitely selective, and trioleins are more readily attacked than dioleoglycerides, and the latter more so than the mono-oleo compounds. Further, the data obtained indicate that a more delicate kind of selective hydrogenation goes on throughout the process, namely, the preferential attack on mixed glycerides containing palmitic groups over those containing only stearic residues. The experimental part of the paper gives the conditions of hydrogenation. The determination of the component fatty acids was made by the method described in several papers, *e.g.* ANALYST, 1929, **54**, 80. In the determination of the fully-saturated glycerides a preliminary separation of part of these was possible from olive oil, by cooling the ethereal solution of the whole products of oxidation to 0° C., and removing the solids by filtration. With cottonseed oils the separation of sodium salts from ether was omitted, owing to the relatively large quantities of palmitic glycerides, and most of the acidic products formed during oxidation were washed from the ethereal solution with dilute aqueous potassium carbonate solution, followed by water. D. G. H.

Effect of Storage on Pyrethrum Flowers. C. B. Gnadinger and C. S. Corl. (*Ind. Eng. Chem.*, 1932, 24, 901–903.)—Commercial pyrethrum flowers are harvested in May and June, and begin to arrive in the United States in August and September. Consequently, the pyrethrum crop of a given year cannot be used as an insecticide until the following year; flowers are, indeed, often carried over for a second year before reaching the user. It has been found that freshly-ground pyrethrum flowers, when stored in containers of different kinds, lose from 30 to 43·6 per cent. of their pyrethrin-content within the first year, and the toxicity towards flies diminishes to approximately the same extent. Examination of powdered and ground flowers stored in tightly closed tins showed that the loss of pyrethrins continues for more than two years, but at a diminishing rate. The pyrethrin content of whole Japanese flowers decreases as the age of the flowers increases. T. H. P.

Corrosion of Bronzes by Vinegar. E. M. Mrak and J. C. Le Roux. (*Ind. Eng. Chem.*, 1932, **24**, 797–799.)—All the bronzes tested corroded considerably under the conditions employed (immersion, aeration and spraying), and the vinegar used became highly contamined with heavy metals. Tin, copper and lead were also attacked by the vinegar, the maximum corrosion being attained in the case of lead, when, in a spraying test, 8826 mgrms. of metal per sq. dm. of surface were dissolved in 100 hours. Lead decreased the resistance of bronze to the action of vinegar, and a bronze containing 25 per cent. of lead lost 2607 mgrms. in weight per sq. dm. in 100 hours when sprayed with vinegar. W. P. S.

Lead from Earthenware Vessels. A. Gronover and E. Wöhnlich. (*Z. Unters. Lebensm.*, 1932, **63**, 623–633.)—Restrictions are under consideration against the importation into Germany of earthenware vessels the glaze of which contains lead which can be dissolved under certain specific conditions by hot 4 per cent. acetic acid in excess of the following limits: for vessels of 0·5 litre capacity and upwards, 2 mgrms. of lead for each litre of capacity; for vessels of less than 0·5 litre capacity, 1 mgrm. of lead. The following method for the determination of the lead is based upon the results of numerous tests of the action of 4 per cent. acetic acid on glazed vessels under different conditions:—The vessel is thoroughly washed out with hot water, and then filled with hot water and placed on a water-bath until it is thoroughly heated throughout. The water is then poured out and the vessel is filled with 4 per cent. of boiling acetic acid, after which it is covered with, for example, a glass plate, and heated for half-an-hour on, or in, a bath of boiling water. The acid liquid is transferred to a flask, and the lead in an aliquot part is determined by Winkler's colorimetric method (*Z. Unters. Lebensm.*, 1923, **45**, 361). If the amount of lead is too large to be suitable for colorimetric determination, a part of the liquid is evaporated to dryness, and the lead is determined by the chromate method (*Arb. Kaiserl. Gesundheitsamt*, 1910, **33**, 240). Vessels of more than 3 litres capacity are filled to three-quarters of their volume with the acetic acid. If the amount of lead found is in excess of the limit, it is advisable to make a check determination in the same manner on the same vessel 24 hours later. S. G. C.

Biochemical

Effects of Carotene and of Vitamin *A* on the Oxidation of Linolic Acid. B. R. Monaghan and F. O. Schmitt. (*J. Biol. Chem.*, 1932, **96**, 387–395.)—In the course of work to determine the possible significance of carotene in the metabolic processes of nerve, certain experiments were carried out *in vitro* to test the effect of carotene on the absorption of oxygen by unsaturated fatty acids. It is shown that carotene, the precursor of vitamin *A* in the animal body, greatly inhibits the absorption of oxygen by linolic acid; in fourteen experiments the average degree of inhibition for the first hour was 51 per cent. Oxidised carotene, on the other hand, slightly accelerates the absorption; in twelve experiments the average acceleration in the first hour was 28 per cent. In two experiments, carotene bleached by heating at 105° C. for 3 hours failed to accelerate the absorption of oxygen by linolic acid, and even inhibited it somewhat; thus this substance behaves differently from carotene which has been allowed to bleach at room temperature in caproic acid. Vitamin *A* in small concentrations may completely inhibit the absorption for some hours. As in the case of carotene, this inhibition ceases when the vitamin is destroyed by oxidation. The unsaponifiable matter of cod-liver oil was the source of the vitamin *A* used in these experiments. There remains the possibility that these effects are due to the presence of some anti-oxidant other than the vitamin, but associated with it and subject to oxidation in a similar manner. The possibility that vitamin *A* may be concerned with phospholipid metabolism is discussed. Mattill (*J. Biol. Chem.*, 1931, **90**, 141; ANALYST, 1931, **56**, 200), Oleovich and Mattill (*J. Biol. Chem.*, 1931, **91**, 105; ANALYST, 1931, **56**, 409) and Olcott and Mattill (*J. Biol. Chem.*, 1931, **93**, 59, 65) studied the effect of a number of substances on the induction period of unsaturated fats. The experiments of the authors are concerned only with the period of rapid oxygen consumption following the induction period, and the results obtained by them with carotene and cod-liver oil extract are not in accord with the interpretations of Mattill and his co-workers. The authors consider that, in measuring the pro- or anti-oxidant activities of a substance which itself is subject to oxidation, it is essential to distinguish between the effects of the original substance and those of the oxidised form. P. H. P.

Stimulation of Yeast Growth by Thallium, A "Bios" Impurity of Asparagine. O. W. Richards. (*J. Biol. Chem.*, 1932, **96**, 405–418.)—When different brands of asparagine are used in the culture medium of Williams (*J. Biol. Chem.*, 1920, **42**, 259), the yield of yeast obtained, conditions otherwise being constant, may vary by 65 per cent. An opportunity occurred to investigate the differences between different asparagines. The differences in the yields of yeast obtained are shown to be due to thallium present as an impurity. Thallium was identified spectroscopically in certain of the asparagines. Asparagine which is further purified by recrystallisation gives less growth of yeast. When the asparagine sold by Eimer and Amend is used in the medium, the addition of 0·001 mgrm. of thallium per c.c. of medium gives an increase of 80 per cent. in the yield of yeast. Greater concentrations are toxic and smaller concentrations give less growth. Concentrations of about 10 mgrms. per c.c. inhibit the growth of the yeast almost completely. Thallium should not be added to the medium when the yeast is to be used as a food for man, because of the extreme toxicity of this element to mammals. Inspection of the literature indicates that thallium may be one of the growth stimulants for yeast that have been referred to as "bios." Elvehjem (*J. Biol. Chem.*, **1931, 90, 111**) showed that the yeast-growth is very poor without the presence of iron and copper. The addition of 0·001 mgrm. of iron per c.c. to a medium containing etiolated yeast gave an increase in growth of nearly 400 per cent. The addition of the same amount of copper increased the yield further, but proportionally less. The inorganic salts and sugar of reagent grade used by the author contain enough iron and copper, as impurities, because on addition of 0·001 mgrm. per c.c. of iron, and of copper in the form of chlorides, there was no increase with the added iron, and slightly less growth when the copper was added. It is believed that attempts to isolate and identify complex organic materials alleged to stimulate the growth of yeast will be premature and unsuccessful until the inorganic food requirements of yeast are known to be supplied completely by culture media. The importance of inorganic foods for the growth of yeast is stressed, and it is suggested that the conflicting observations found in the literature on the growth of yeast are due partly to inadequate culture media and inconstant conditions of growth. P. H. P.

Toxicological and Forensic

Reagent facilitating the Formation of Haemin Crystals from Blood. G. Bertrand. (*Ann. Chim. Anal.*, 1932, **14**, 353–354.)—This reagent is made by dissolving 1 grm. of crystallised magnesium chloride in 1 grm. of water, adding 5 grms. of glycerol (30 per cent.), and then 20 grms. of glacial acetic acid, and mixing; it keeps unchanged in a corked vessel. A small quantity of residue obtained by evaporating the haemoglobin solution is treated with a drop of the reagent and covered with a microscope cover-glass. To examine blood which has dried on a support from which it cannot be completely detached, a fine particle is transferred to a slide and a drop of the reagent is added. The preparation is warmed for a few seconds over a small flame. Microscopic examination then usually reveals crystals of haemin, the number of these increasing if the slide is again heated. Dried blood gradually swells under the action of the reagent, and the first haemin crystals appear in the outside layers. T. H. P.

Organic Analysis

Application of Chromic Oxidation to Certain Alcohols. L. Semichon and M. Flanzy. (*Compt. rend.*, 1932, **195**, 254–256.)—In the study of this oxidation, 5 c.c. of solution, containing 1 mgrm.-molecule of the alcohol were treated at 15° C. with a solution of 0·68 grm. of potassium dichromate in 20 grms. of water and 10 c.c. of sulphuric acid (sp.gr. 1·71). Methyl alcohol is oxidised completely to carbon dioxide and water after 1 hour. Ethyl and other normal alcohols (propyl, butyl, amyl, hexyl, and heptyl) are all oxidised quantitatively to the corresponding acids in periods varying from 10 minutes (ethyl) to 90 minutes; the acids formed are not attacked further, even after 20 hours. Isopropyl and secondary butyl alcohols, and methylpropylcarbinol give the corresponding ketones quantitatively within 1 hour; acetone is not attacked in 2 hours, and the butyl ketone undergoes very slight attack in 90 minutes. When 5 c.c. of solution containing 0·076 grm. of acetone are heated at 100° C. for 1 hour with a solution of 0·525 grm. of chromic oxide in 5 grms. of water and 5 c.c. of sulphuric acid (sp.gr. 1·71) the acetone is transformed completely into acetic acid. The homologous ketones undergo similar conversion into acetic acid under these conditions. To determine the primary and secondary alcohols present in a wine, this is oxidised in the cold, and the fatty acids and ketones are distilled off in a current of steam; the distillate is then neutralised and the ketones are distilled off alone.

Trimethylcarbinol is not completely oxidised in the cold in 125 hours, but, in concentrated solution, it is transformed quantitatively into acetic acid at 100° C., isobutyric acid, acetone, and propionic acid being formed as intermediate products in the order given. At 15° C., ethylene, propylene and butylene glycols are oxidised (similarly to the primary alcohols) to the corresponding acids. Chromic oxidation of glycerol, erythritol, mannitol, dextrose, laevulose, sucrose, dextrin, or starch yields appreciable amounts of formaldehyde. With the weak oxidising mixture (see above), glycerol is converted quantitatively into carbon dioxide and water in less than 1 hour, and with other polyhydric alcohols containing no methyl group, the oxidation also proceeds as far as carbon dioxide and water. In general, if an alcohol molecule contains one or more methyl groups, the stronger oxidising mixture converts it quantitatively into acetic acid in less than 1 hour at 100° C. If methyl groups are absent, but the molecule contains several CH_2 groups linked together, succinic or a homologous acid is formed quantitatively under these conditions. T. H. P.

Analytical Reactions of Alkyl Mercaptans in Benzene Solution. J. R. Sampey and E. E. Reid. (*J. Amer. Chem. Soc.*, 1932, **54**, 3404–3409.)—In determining mercaptans by iodimetry (*J. Amer. Chem. Soc.*, 1921, **43**, 119) in benzene solutions it is necessary to allow 3 hours in the case of normal mercaptans for the reaction to go to completion, and for long-chained secondary mercaptans 24 hours' contact in the dark is necessary. An intermediate addition-compound between the iodine and mercaptan is apparently formed, but this question is being further investigated. Modifications of this method were studied: (1) *Hydriodic acid method.*—Fifty c.c. of a benzene solution of the mercaptan are left to stand with excess of iodine solution until oxidation is complete; the excess of iodine is removed with thiosulphate solution, the aqueous and benzene layers are separated, the latter is washed with 60 c.c. of water in three portions, and the hydriodic acid in the aqueous layer and washings is titrated with 0·025 *N* sodium hydroxide solution with bromcresol purple or purified litmus as indicator. The method is not quite as accurate as the iodine method. (2) *Mercuric chloride method.*—Fifty c.c. of a benzene solution of the mercaptan are shaken vigorously for 3 minutes with 25 c.c. of 1 per cent. mercuric chloride solution. If no (or very slight) precipitation occurs, the hydrochloric acid is washed from the benzene layer with three 25-c.c. portions of water, and the acid in the aqueous layer and washings is titrated with 0·025 *N* sodium hydroxide solution, methyl orange or red being used as indicator. If a heavy precipitate is formed the alkali is slowly added to the mixture without separation into layers, with frequent shaking, methyl orange being used as indicator. Results are on the low side, but a correction factor may be found by standardising a volume of sodium hydroxide approximately the same as that required for the titration against 0·025 *N* alkali with the same indicator. Both these methods may be used for mercaptans in naphtha solution which has been freed from unsaturated hydrocarbons, but they break down in the presence of unsaturated hydrocarbons. D. G. H.

Determination of Lactic Acid in Vegetable Tan Liquors. J. H. Highberger and D. L. Youel. (*J. Amer. Leather Chem. Assoc.*, 1932, **27**, 343.)—The method consists in boiling the tannin-free liquors with acid and potassium permanganate, by which means any lactic acid is oxidised to acetaldehyde and, after being distilled off, is titrated with standard iodine solution. The oxidation takes place in a 500-c.c. Kjeldahl flask, the stopper of which has two holes, through one of which passes a thistle-funnel for adding the permanganate solution, whilst the other is for an internally-cooled reflux condenser. The latter is connected through a small receiving flask with an absorption-tower, the top of which leads to a trap and water pump.

Ten c.c. of the tan liquor, diluted to 50 c.c., are thoroughly shaken with a small quantity of basic lead carbonate. Ten to 15 c.c. of 10 per cent. lead acetate solution are slowly added to the settled mixture, and the whole is again shaken, allowed to subside and filtered. The residue is washed five or six times with hot water, and the filtrate and washings are saturated with calcium hydroxide (about 0·75 grm.), and treated with about 0·3 grm. of pulverised copper sulphate crystals. After 20 minutes the precipitate is filtered off and washed with hot water, and the solution and washings are transferred to the Kjeldahl flask, together with 25 to 30 c.c. of 10 *N* sulphuric acid containing 76 grms. of manganous sulphate per litre. The solution is gently boiled, while slight suction is applied through the empty receiving flask for at least 3 minutes. The suction is stopped, the burner is removed, and the receiving flask is replaced by one containing 20 c.c. of 0·15 to 0·20 *M* sodium bisulphite solution. Gentle suction and boiling are renewed, after which 0·1 *N* potassium permanganate solution is run in at such a rate that the solution in the Kjeldahl flask is kept just free from becoming pink. As soon as brown manganese dioxide separates, addition of permanganate is stopped, and the boiling and aspiration are continued for 5 to 10 minutes, after which the absorption-tower is washed down. Starch indicator is added to the receiving flask, and 0·1 *N* iodine solution is run in until the end-point is approached, the final adjustment being made with 0·0222 *N* iodine solution. About 0·5 grm. of solid sodium bicarbonate is gradually added, discharging the blue colour, and the final titration is carried out with the dilute iodine solution (1 c.c. = 0·9 mgrm. of lactic acid).

By this method interfering substances which yield bisulphite-binding materials on oxidation are removed; oxidisable substances not so removed yield no bisulphite-binding material on oxidation and occasion no loss of lactic acid. The results give the total lactic radical, rather than lactic acid only. Rocker liquors were found to contain 0·15 to 0·4 grm. per 100 c.c. of lactic acid radicle. R. F. I.

Comparison of Chestnut Bark and Chestnut Wood Extracts. A. Ponte. (*J. Inter. Soc. Leather Trades Chem.*, 1932, 16, 394).—Extracts of chestnut wood contain only a small amount of catechol tan [about 4·3 per cent. of the total tan as determined by the formaldehyde and hydrochloric acid method of Ponte and Gualdi (*Boll. Uff. R. Staz. Sper. Ind. Pelli.*, Sept., 1931)], whereas bark extracts contain nearly 25 per cent. The latter contain more mineral matter, iron, copper and calcium, than the former. Thus, solutions (25° Bé) gave the following results:

	Ash Per Cent.	Calcium oxide Per Cent.	Iron Per Cent.	Copper Per Cent.	p_H of solution
Bark	1·55	0·43	0·013	0·144	3·7
Wood (de-barked)	0·27	0·08	0·007	0·008	2·7

The high copper-content is attributed to the acidity of the liquors in the autoclaves and, to a less extent, in the evaporators. The fact that more copper is present in the less acid material is explained by assuming that the presence of more mineral ash is indicative of a higher content of salts of oxyacids, the action of which on the autoclave is intensified by the oxygen of the air. The low p_H value of the wood extract is attributed to acetic acid formed by fermentation in the wood stacks before autoclaving. The general conclusion is that chestnut woods should be de-barked before being extracted. R. F. I.

Quantitative Determination of Cotton, Wool, Silk and Artificial Silks in Mixed Textiles. P. Krais and H. Markert. (*J. Text. Inst.*, 1932, 23, 213.)—The material under examination must first be freed from any non-fibrous matter, such as oil, fat, finishing or waterproofing material, by treatment with ether, alcohol, enzymes, dilute acids, or dilute ammonia, followed by 24 hours' exposure in an atmosphere of 60 to 65 per cent. relative humidity. The general type of fibres present is ascertained by the use of the microscope. The quantitative separation of the various fibres is carried out as follows:—The acetate rayon may be removed by treatment with acetone. Five grms. of the sample are boiled with 150 c.c. of 2 per cent. sodium hydroxide solution for half-an-hour under a reflux condenser, filtered on to a fine bronze sieve, washed, dried, conditioned at 60 to 65 per cent. relative humidity, and weighed. Wool and silk are dissolved; cotton, flax and ramie are undissolved. Five grms. of the sample are placed in a glass-stoppered flask, 150 c.c. of 80 per cent. sulphuric acid are added, and the flask is shaken vigorously for 15 minutes, and then every quarter of an hour during 3 to 4 hours. The mixture is filtered, washed and dried as before. All vegetable fibres are removed, but wool and silk remain. Two hundred c.c. of calcium thiocyanate solution (1000 grms. per litre) are placed in a wide-mouthed flask (fitted with a stirring device), and warmed to 70° C., and 1·5 grm. of the sample is added. The whole is heated for 1 hour in a boiling water-bath, with constant stirring, after which the mixture is filtered, etc., as before. This treatment removes silk, cellulose and acetate rayons, but not cotton or wool. A table is given showing the correction factors which should be taken into account with each treatment. R. F. I.

Drying Rates of Synthetic Resins with Drying Oils. I. China Wood Oil. C. A. Thomas and P. E. Marling. (*Ind. Eng. Chem.*, 1932, 24, 871–873.)—The drying of commercially-pure China wood oil is accelerated by additions of small quantities of β-naphthol if the drying is carried out under mercury-arc light, or in sunlight, or at high temperatures. The presence of synthetic resins markedly influences the rate of drying of the oil, the rate of drying of China wood oil varnishes depending largely on the type of the resin used. With varnishes prepared with natural or synthetic resins, the drying may or may not be retarded by β-naphthol. In general, however, the drying of neutral resin varnishes is accelerated by addition of the naphthol, and this effect is cumulative when β-naphthol is used in conjunction with metal dryers. T. H. P.

Determination of Small Amounts of Methyl Chloride in Air. F. A. Patty, H. H. Schrenk and W. P. Yant. (*Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 259–262.)—The method is very similar to that used for the determination of total sulphur in fuel gases. The air containing the methyl chloride is mixed with natural gas and burned in a micro-burner, and the halogen products are made to combine with ammonia from ammonium carbonate cubes round the burner, and also with ammonium hydroxide formed by the ammonia from the ammonium carbonate and the water in the products of the combustion of the gas. The chlorides, some of which are deposited on the upper part of the trumpet tube surrounding the special burner, and the rest from the marble-filled absorption tower, are collected and determined by the Volhard method. The silver chloride is removed by filtration prior to the thiocyanate titration. With amounts of methyl chloride ranging from 20 to 30 mgrms. the accuracy of the method is mostly about 0·5 per cent., and always within 1 per cent., and with amounts as low as 12 mgrms. it is mostly about 1 per cent., and always within 2 per cent. Owing to the solubility of methyl chloride in water, water should not be used as the displacing medium for the most accurate work, although for practical health investigations it may be used if not agitated a great deal or left in contact with the gas-laden air. The same apparatus was also used to determine dichlorofluoromethane and dichlorodifluoromethane in concentrations of 2 and 20 per cent., samples being taken over mercury and diluted with air before burning. D. G. H.

Inorganic Analysis

[Determination of] Small Amounts of Sulphur Dioxide in the Atmosphere. S. W. Griffin and W. W. Skinner. (*Ind. Eng. Chem.*, 1932, 24, 862–867.)—Various modifications in the iodimetric process, and also a field-testing outfit, are described. Volumes of the air (measured in a meter) are passed through scrubbers or absorbers which contain very dilute iodine solution (about 0·00003 *N*) in aqueous potassium iodide solution, together with a small amount of starch (25 c.c. of 0·2 per cent. soluble starch solution per litre of the absorbing solution). One scrubber removes over 90 per cent. of the gas from air containing sulphur dioxide in the concentrations usually encountered, and this is regarded as sufficient, the result being corrected for the known efficiency of the particular scrubber under the prevailing conditions.

The air is passed through 100 c.c. of the starch-iodine solution at the rate of 7·5 litres per minute for four minutes, the volume of the air passed being corrected for temperature and pressure. The solution is at once transferred to a 250-c.c. flask, and, after addition of a pinch of sodium bicarbonate, titrated with about 0·0013 *N* sodium thiosulphate solution until a predetermined pale blue colour appears. This standard blue colour is obtained by dissolving commercial dyes, such as Diamond dyes, in water, and adding a trace of Indian ink to produce turbidity similar to that caused by the colloidal starch particles; the colour of such a solution is quite fast, and the standard may be used in the field for some weeks.

The absorbing solution is somewhat unstable towards light and loses a proportion of its iodine when pure air is bubbled through it. As this proportion depends on a number of factors, correction is impracticable, and it is essential that blank tests be carried out either at the same time as, or interspersed with, the actual tests. In these blank tests the air passing to the iodine absorbent is first passed through a tower, 12 inches in height and 1·5 inch in diameter, packed with loose, friable soda-lime; all glass and rubber connections used should be at least 0·5 inch in diameter, as narrow connections interfere with the accuracy of flow-meter readings.

For the field tests, air-suction is provided by either: (1) the intake manifold of the engine of an automobile or the suction tube leading to the wind-screen wiper, or (2) a rotary blower, worked electrically or by hand. In cold weather, the absorbing and measuring apparatus may be placed inside the car and the air drawn in through a glass or tin tube reaching some distance away from the machine. Under usual field conditions the method can detect 0·02 parts of SO_2 per million of air. Mechanically the method is limited by the accuracy of the measurement of the volume of air, namely, ± 2·5 per cent. The method is specific for the determination of sulphur dioxide from smelting furnaces, as these do not normally yield hydrogen sulphide. Sulphur trioxide in traces has no effect on the iodine solution. When dust or pollen appear to be present in appreciable amounts in the air, the air-inlet of the flow-meter should be protected by a filter, which is suitably prepared by sucking a thin mat of asbestos or cotton linters on to a fritted glass base or funnel. The first few readings made when such a filter is inserted should be discarded. The method has been used in connection with fumigating tests with sulphur dioxide. T. H. P.

Determination of Silver in Cyanide Solutions. A. Wogrinz. (*Z. anal. Chem.*, 1932, 89, 120–121.)—The measured solution in a conical flask is diluted and treated with 3 grms. of potassium hydroxide and a pinch of oil-free aluminium bronze powder; foaming and hydrogen evolution indicate complete precipitation of the silver. The precipitate is collected on a porous crucible, carefully washed, returned to the flask, and dissolved in chlorine-free nitric acid. The silver solution is titrated with thiocyanate (Volhard). The author finds that gravimetric determination of silver in cyanide solution, *i.e.* precipitation with hydrochloric acid and ignition of the precipitate in hydrogen, does not give pure silver, the results being always high. W. R. S.

Separation of Arsenic Trichloride and Germanium Tetrachloride. E. R. Allison and J. H. Müller. (*J. Amer. Chem. Soc.*, 1932, **54**, 2833–2840.)—Germanic chloride is practically insoluble, whilst arsenious chloride is very soluble, in strong hydrochloric acid. The authors studied the distribution of arsenious chloride between germanic chloride and hydrochloric acid, and succeeded in freeing germanic chloride from arsenic by repeated shaking with strong hydrochloric acid in a separating funnel. Antimonic, stannic, and titanic chlorides can be separated from germanic chloride by a single extraction with hydrochloric acid, which is explained by the formation of the complex chloro-acids. Arsenious chloride does not form a compound of this type. W. R. S.

Gravimetric Determination of Tellurium. O. E. Clauder. (*Z. anal. Chem.*, 1932, **89**, 270–282.)—Tellurium, as usually obtained in analysis, is an amorphous precipitate, the easy oxidisability of which complicates its determination. Accurate results are obtained if the element is precipitated in a crystalline condition; this can be achieved by the use of hypophosphorous or sulphurous acids, salts of hydrazine, semicarbazide, or hydroxylamine, or titanous chloride, provided the tellurium solution contains 15 to 20 per cent. of hydrochloric acid, with other conditions as follows: Absence, or almost complete absence, of sulphuric and organic acids; the reducing agent should be added in dilute (5 to 10 per cent.) solution all at once, and in moderate excess, to the cold tellurium solution (bulk, 100 c.c.), which is then warmed by being placed in boiling-hot water. The crystalline precipitate can be dried in a very short time, no oxidation taking place. Potassium hypophosphite is specially recommended as precipitant; 20 c.c. of a 5 per cent. solution were used for 0·02 to 0·3 grm. of tellurium. The cold solution (50 c.c.), placed in hot water, is agitated for 45 minutes by a brisk current of air, and diluted to 100 c.c. The precipitate is collected in a porous glass crucible and washed in succession with 50 c.c. of N hydrochloric acid, 25 c.c. of water, and 10 c.c. of alcohol; air is aspirated for 10 minutes through the crucible, which is then dried for one hour at 130° C.

If bismuth is present, the tellurium should be washed with 25 c.c. of a stronger (3 N) acid; the quantity of bismuth present should be less than 1·5 grm. Antimony should not exceed 0·75 grm.; the washing is conducted as for bismuth. Copper in quantities below 0·5 grm. is not precipitated by hypophosphite at the prescribed acidity. Lead as chloride contaminates the precipitate; in such a case the precipitate is dissolved in nitric acid, the solution is evaporated twice with hydrochloric acid, and the precipitation is repeated. Iron, cobalt, and nickel do not interfere.

The precipitation of tellurium dioxide by the method of Browning and Flint requires practice, as the precipitate is soluble in acids, as well as in ammonia. The author recommends the use of hexamethylenetetramine for the adjustment of the p_H. The solution of tellurous acid, containing 1 grm. at least of ammonium chloride, is treated with ammonia to permanent cloudiness, then with 10 c.c. of *N* hydrochloric acid, diluted to 100 c.c., and boiled. It is precipitated while boiling, with 10 c.c. of a 20 per cent. solution of the base, added drop by drop. After standing overnight the precipitate is collected in a porous glass crucible and washed with 50 c.c. of water, followed by 5 c.c. of alcohol; it is dried at 130° C. for an hour, then by suction with air dried over calcium chloride for 5 minutes, and weighed as TeO_2. The method effects a separation of tellurium from selenium.

W. R. S.

Determination of Cobalt in Magnet and High-Speed Tool Steels. J. I. Hoffman. (*Bur. of Standards J. Research*, 1932, 8, 659–668.)—In this method the bulk of the iron is removed from a solution of the steel by means of ether; the cobalt is separated from chromium, etc., by precipitation with sodium hydroxide and peroxide; copper and the remaining iron, etc., are separated from the cobalt by precipitation with cupferron; the cobalt is finally precipitated with α-nitroso-β-naphthol. *Method.*—A 1-grm. sample contained in a 400-c.c. beaker is decomposed by heating with 20 c.c. of dilute hydrochloric acid (2:1); 2 c.c. of dilute nitric acid (1:1) are added, and the liquid is boiled for 2 to 3 minutes and then evaporated to a volume of 5 c.c. Any separated tungstic acid is ignored. The liquid is transferred, with the aid of dilute hydrochloric acid (1:1), to a separating funnel (the total volume of the liquid should not exceed 35 c.c.), and cooled to about 5° C.; 50 c.c. of ether are added, and the mixture is shaken for 1 minute. The lower layer is run off in to another separating funnel; the ethereal extract is washed with 10 c.c. of dilute hydrochloric acid (1:1), and the washing liquid is run off into the second funnel. The contents of this funnel are extracted with a further 50 c.c. of ether, the ethereal layer being washed as before; the aqueous liquids are collected in the original beaker, heated gently to expel dissolved ether, and finally evaporated almost to dryness. Fifteen c.c. of dilute nitric acid (2:1) are added, and the whole is evaporated just to dryness; the residue is dissolved in 50 c.c. of dilute hydrochloric acid (5 per cent.). An aliquot portion of this solution, containing 0·1 grm. or less of cobalt, is poured into 150 c.c. of sodium hydroxide solution (5 per cent.), to which have been added 2 grms. of sodium peroxide; the mixture is heated on a steam-bath for half-an-hour to destroy the excess of peroxide, allowed to cool, and the precipitate is filtered off and washed with hot water. The paper and precipitate are digested with 15 c.c. of hot dilute hydrochloric acid (2:1) until the precipitate has dissolved; the paper is stirred to a pulp and 150 c.c. of water are added. The solution is neutralised with ammonia (with litmus as indicator); 5 c.c. of concentrated hydrochloric acid are added, the solution is cooled to about 10° C., and a slight excess of cupferron is added (a total of 10 c.c. of 6 per cent. solution is normally sufficient). The precipitate is filtered off after 10 minutes, washed with a cold, very dilute solution of cupferron in 1 per cent. hydrochloric acid, and rejected. The filtrate is diluted to about 400 c.c., and 15 c.c. of concentrated hydrochloric acid are added, followed by an excess of a solution of α-nitroso-β-naphthol in acetic acid. The liquid is heated to 60°–70° C. for 20 minutes and filtered; the precipitate is washed with hot dilute hydrochloric acid (1:3), and, finally, with hot water, dried, "burnt off" together with the filter paper, ignited to constant weight at 750–850° C., and weighed as Co_3O_4. In all accurate work in which more than 0·01 per cent. of cobalt is involved, the oxide must be reduced in hydrogen and the cobalt weighed as metal. When more than 0·1 per cent. of copper is present in the steel, the cobalt metal thus obtained may contain a few tenths of a mgrm. of copper; a correction may be made for this by dissolving the cobalt in hydrochloric acid, diluting the solution and precipitating with hydrogen sulphide, the precipitate of copper sulphide being then ignited, the residue dissolved in nitric acid, and the copper determined colorimetrically with ammonia. The results of test experiments were very good when the cobalt was determined as the metal, but were slightly low when calculated from the weighing of Co_3O_4. S. G. C.

Determination of Titanium in Alloy Steels. J. Arend. (*Z. anal. Chem.*, 1932, **89**, 96–100.)—The drillings (10 grms.) are dissolved in 150 c.c. of hydrochloric acid (1:5 water) in a current of carbon dioxide, the bulk of the acid is neutralised with sodium carbonate, and the solution is diluted to 300 c.c. and treated with barium carbonate emulsion in slight excess, all in an atmosphere of carbon dioxide. After half-an-hour's settling, the precipitate is collected and washed with acetic acid (1:2 water). The precipitate is ignited and fused with carbonate-nitrate mixture, borax being added if alumina is present. The melt is extracted with water, and the solution (containing a little silicate, chromate, vanadate, tungstate, phosphate) is filtered.. The washed residue is ignited and again fused with carbonate The product is dissolved in strong hydrochloric acid, and a little water is gradually added. The solution is treated with tartaric acid, made ammoniacal, heated, and any copper and a little iron are precipitated with hydrogen sulphide. The filtrate from the sulphides contains titanium only, which is recovered by means of *o*-hydroxyquinoline (ANALYST, 1930, **55**, 596). W. R. S.

Separation of Caesium from other Alkali Metals. N. A. Tananaeff and E. P. Harmasch. (*Z. anal. Chem.*, 1932, **89**, 256–262.)—Caesium iodobismuthate, $Cs_3Bi_2I_9$ (Wells's salt) forms sparingly-soluble blood-red hexagonal crystals, whilst none of the other alkali metals yields such a compound. The reaction can be used fór the separation of caesium from the other alkali metals, with a negative error of one per cent. The saturated solution of the chlorides is treated with a hot solution of iodobismuthic acid (3 times the required amount of bismuth iodide dissolved in a minimum of hydriodic acid), the liquid being carefully stirred so as to prevent the formation of lumps of precipitate. After some minutes' stirring the beaker is placed in cold water for 20 minutes; the precipitate is collected in a porous glass crucible, washed with a saturated solution of the complex caesium salt and then with water cooled below 7° C., and dried to constant weight at 140° to 150° C. If the washing is conducted with cold water only (to disappearance of the bismuth reaction), the results are slightly lower than 99 per cent. Cs factor, 0·2038. W. R. S.

Test for Iodide. C. I. Kruisheer. (*Z. anal. Chem.*, 1932, **89**, 196–197.) —The aqueous solution of an iodide, treated with an equal volume of 25 per cent. hydrochloric acid and strong sodium sulphite or bisulphite solution, gives a yellow coloration. If the liquid is shaken with amyl alcohol the latter will assume a yellow colour. The reaction detects 0·0005 grm. of iodine in 2 c.c. of the original liquid; bromides and chlorides do not interfere, nor do the common acid ions. Iodate, hypoiodite, and free iodine give the reaction. If the solution contains coloured organic compounds which would colour the alcohol, they must first be removed by repeated extraction with the solvent until it remains colourless.

W. R. S.

Microchemical

Microchemical Detection of Vanillin and Piperonal. M. Wagenaar. (*Mikrochem.*, 1932, **11**, 135–138.)—*Vanillin.*—Vanillin forms colourless monoclinic prisms, slightly soluble in cold water, readily soluble in most organic solvents. It sublimes readily, forming drops which dissolve easily in water containing some acetone, and, on evaporation, good crystals are formed. The smallest amount recognisable is 1 mgrm. A precipitation test consists in diluting the solution of vanillin in water containing acetone, the vanillin then crystallising in needles having an acute angle of 63°. The smallest amount recognisable is 0·5 mgrm. *Crystalline compounds.*—(1) With concentrated nitric acid vanillin is nitrated, the resulting compound forming good crystals about 0·1 mm. long. The smallest amount recognisable is 0·5 mgrm. (2) With ferric chloride and other weak oxidising agents (such as gold chloride, potassium or ammonium dichromate in dilute sulphuric acid) crystalline oxidation products are produced which are similar, but not identical. That obtained with ferric chloride melts at 302–305° C. (3) Griebel's test (*Mikrochem.*, 1931, **9**, 311), in which a drop of 3 per cent. hydrogen peroxide and a small drop of 25 per cent. hydrochloric acid are used and the mixture is allowed to evaporate, gives hair-like, dark crystals, melting at about 200° C. Perborates or magnesium peroxide may be used instead of hydrogen peroxide, but not hypochlorites, perchlorates or nitrites.

Piperonal.—Piperonal is slightly soluble in water, and very soluble in organic solvents, and crystallises in long prisms with pyramid-shaped ends. *Precipitation.*—Piperonal behaves in the same way as vanillin in sublimation and precipitation tests. *Crystalline compounds.*—(1) Only in concentrated form (sp.gr. 1·5) does nitric acid dissolve piperonal, giving a yellow colour. The nitrated product crystallises on cooling. The smallest amount recognisable is 1 mgrm. (2) With bromine water hair-like crystals of the brominated aldehyde are formed. The smallest amount recognisable is 0·1 mgrm. (3) With iodine in potassium iodide solution good crystals are obtained. A few crystals of piperonal are stirred into a drop of iodine solution, and the precipitate is dissolved in a few drops of acetone. After evaporation of the solvent the periodide crystallises out in black dichroic hair-like crystals. The smallest amount recognisable is 0·1 mgrm. (4) With phenylhydrazine a hydrazone is obtained, which crystallises from alcohol or acetone, but this reaction is not very distinctive.

J. W. B.

Rinnmann's Green Test for Zinc. A. A. Benedetti-Pichler. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 336–337.)—The reagent paper is prepared by soaking "ash-free" filter paper in a solution of 4 grms. of potassium cobalticyanide and 1 grm. of potassium chlorate in 100 c.c. of water, and drying. When slightly heated such paper takes fire, leaving a black ash consisting mainly of cobaltous oxide. A drop of the solution to be tested is transferred to the centre of the paper, about 2 cm. square, and, after absorption of the liquid, the paper is held high above a Bunsen flame. A yellow line first appears along the outline of the drop, the centre then turning brown. The paper is then lighted, and the ash is examined on a porcelain plate. If zinc was present, a disc of green ash will be seen where the drop of solution was added, surrounded by a circular zone containing very little ash. For micro-technique the size of the cobalticyanide paper may be diminished to less than a quarter, and the test solution drawn into the paper by means of a micro-pipette with fine bore. The final appearance of the test will depend not only on the absolute amount of zinc present, but also on the concentration and volume of the zinc solution, etc., and with very small amounts a small thread or delicate network of green fibres only may be seen under the microscope. With the macro-technique the limit of concentration is 1 mgrm. of zinc per c.c., and the limit of identification is 0·05 mgrm. of zinc, and with the micro-method, the limit of concentration is 0·4 mgrm. of zinc per c.c., and the limit of identification is 0·0006 mgrm. The limit proportions for the presence of other metals are: Zinc : cadmium, 1 : 5; zinc : manganese, 10 : 1; zinc : cobalt, 2 : 1; zinc : nickel, 1 : 1; zinc : titanium, 1 : 1; zinc : aluminium, 1 : 2. D. G. H.

Micro-vacuum Distillation. R. A. Smith. (*Mikrochem.*, 1932, **11**, 221–226.)—A simple apparatus for fractional micro-vacuum distillation, with thermo-couple temperature reading, is made from a test-tube (1 cm. diameter) or glass tubing of similar bore. The test-tube is drawn out to capillaries of 1 to 2 mm. inner diameter and 25 to 30 cm. long, each capillary being separated from the next by a short bulb of the original tubing. Three or four bulbs can be formed from one test-tube; the number of bulbs depends on the number of fractions required from the liquid. The mouth of the test-tube is left intact, and can be attached to the vacuum-pump. The other end of the apparatus consists of a capillary tube. The apparatus is bent so that the bulb next to the end capillary is vertical, and the others horizontal, each suitable for immersion in a bath. A thermo-couple (Constantin-nichrome, 0·0125 mm. in diameter) is attached to the vertical bulb. The liquid is introduced by means of the suction-pump through the end capillary, which is then drawn out as a fine tip. By suitable arrangement of heating baths each fraction can be obtained in a different bulb. When the distillation is complete the bulbs can be sealed separately. J. W. B.

Physical Methods, Apparatus, etc.

Optical Determination of Sodium Nitrite. K. Weber. (*Chem.-Ztg.*, 1932, **56**, 642–643.)—Unlike all other colourless inorganic salts, sodium nitrite exhibits marked absorption of ultra-violet light of wave-length between 300 and 400$m\mu$, the absorption following the law, $A=100(1-10^{-\epsilon cp})$, A being the percentage of the light absorbed, p the thickness of the layer in cm., and c the concentration of the sodium nitrite in grms. per 100 c.c. A curve is given, showing the variation, with concentration, of the absorption of a 2-cm. layer of the nitrite solution, for light of $386 m\mu$ wave-length. To determine the content of sodium nitrite in a pickling salt, 10 grms. of the salt, which should contain from 0·5 to 0·6 per cent. of the nitrite, are dissolved in water, and the solution is made up to 100 c.c. The ultra-violet absorption ($386 m\mu$) is then measured by means of Plotnikow's fluorometer (*Z. Elektrochem.*, 1929, **35**, 432), and the content of sodium nitrite is read off from the curve. With practice, the absorption can be measured to within 1 per cent., this corresponding with an accuracy of 0·015 per cent. for the dry salt; the measurement occupies about 5 minutes. In laboratories where a quartz lamp, a polarisation colorimeter, a step-photometer, etc., are available, a fluorometer can be easily assembled, a suitable fluorescing substance being a 0·1 per cent. solution of quinine sulphate in *N* sulphuric acid. T. H. P.

Spontaneous Ignition of Beech-Wood Charcoal Dust. E. Möhlau. (*Chem.-Ztg.*, 1932, **56**, 581–582.)—The spontaneous ignition which is proved to occur when finely divided carbonaceous matter is stored in bulk has been studied in the case of beech-wood charcoal. By the method of Dennstedt (*Z. angew. Chem.*, 1912, **28**, 2627; *Chem.-Ztg.*, 1919, 402), as modified by Mildner (*Braunkohlarch.*, 1927, **15**, 42), in which a current of oxygen is made to pass through a column of the powder kept under controlled conditions of temperature, the following results were obtained:

State of division	Commencement of spontaneous rise of temperature °C.	Ignition point °C.	Time of burning	
			at 120° C. Minutes	at 130° C. Minutes
Coarser grains	110–120	180	30	22
Finest grains	95–100	170	30	16

The temperature of spontaneous ignition of beech-wood charcoal dust is stated to be near to that already established for lignite dust. On the basis of the above results the author considers that a rise in temperature to 50° C. within a mass of the material would definitely indicate the onset of auto-oxidation which would ultimately lead to spontaneous ignition, and, therefore, proposes that when large quantities of this material are stored, some form of automatic temperature indicator should be employed, in order to give warning in time for preventive measures (which are not detailed) to be taken. S. G. C.

Reviews

ORGANIC SYNTHESES. Collective Volume I. Editor-in-Chief: HENRY GILMAN. Pp. ix+564. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. Price 37s. 6d. net.

To those who, during the past years, have used the previous nine annual publications of "Satisfactory Methods for the Preparation of Organic Compounds," the issue of the collective volume, with its copious indexes, is indeed welcome. The new work is more than a reprint of the separate books, for the whole subject matter has been recast. In the separate volumes one occasionally finds notes referring to newly-discovered improvements in previously published methods; in the Collective Volume these are either incorporated in the process to which they belong or are inserted in their proper places. The 260 or so preparations described are arranged in alphabetical order.

As in the original publications, each preparation is set out under the headings: (i) Scheme or equation representing the reactions; (ii) details of procedure; (iii) notes; (iv) summary of methods available; and (v) original references. Since the object of the authors is to provide, after practical test, details for obtaining the maximum yield in the preparations described, no theoretical discussions, such as are a feature of books like Gattermann's *Praxis des organischen Chemikers*, are to be found. In passing, it may be mentioned that some of the formulae used are a little difficult to recognise; thus, $HO_2CCH_2C(OH)(CO_2H)CH_2CO_2H$ for citric acid would be improved by a few full stops. There seems to be no reason why such formulae should not be written structurally.

The range of preparations is extensive, and those engaged in organic research or the manufacture of fine chemicals will do well to consult this book. For the analyst, however, only a few of the preparations are of interest, for, while details are given for the preparation of cupferron, isatin, aurin-tricarboxylic acid and α-nitroso-β-naphthol, no mention is made of 8-hydroxyquinoline, dimethylglyoxime, or diethyl-dithio-carbamate. Only one indicator, *viz.* methyl red, is mentioned. Among the substances of general interest which are treated in detail may be mentioned ketene, nitromethane and *p*-nitrobenzoyl chloride.

The book is well bound and clearly printed; the illustrations, though few in number, are excellent; and the five thumb-indexes make it extremely easy to use. The indexes are under the following headings: (i) Type of Reaction; (ii) Type of Compound; (iii) Formula (after the style of Richter's Lexicon); (iv) Illustration; and (v) General.

Collective Volume I is up to date, for, during its compilation, the literature up to December 1, 1931 has been consulted. The authors are to be congratulated on having given to the world a set of thoroughly reliable directions for the preparation of what may be regarded as "key-compounds" in organic chemistry, and it is with some impatience that we realise that Collective Volume II cannot be published before 1942! Nevertheless, in the meantime, all whose work, from whatever point of view, is connected with the preparation of organic compounds should obtain a copy of Volume I. HAROLD TOMS

THE SCIENTIFIC PRINCIPLES OF PETROLEUM TECHNOLOGY. By Dr. LEO GURWITSCH and HAROLD MOORE. Pp. xii+572, lx plates. London: Chapman & Hall, Ltd. 1932.

The translation by Mr. Harold Moore of Professor Gurwitsch's book has become greatly enhanced in value by the new edition, containing the latest results of modern investigations.

The book is divided into three parts: I, Chemistry and Physics; II, Manufacture; and III, Products.

The first part, on chemistry and physics, explains the scientific facts regarding petroleum and its fractions. The action of oxygen and oxidising agents is also dealt with at length (40 pp.). The chemistry of oxygen, sulphur and nitrogen compounds contained in petroleum oils is dealt with more briefly. Of special interest is a fairly full table showing the sulphur-contents of crude oils from North American sources. The section on natural gas could, perhaps, have been expanded, since the technique used in the recovery of natural gas is now becoming more widely applied.

The section on physics deals with specific gravity and viscosity, surface tension, and the optical, electrical and thermal properties of oils. The section on the power-factor of electrical insulating oils is a new feature which should be of considerable value.

Sections C and D form an interesting and concise statement of the differences which distinguish petroleums obtained from different sources, together with a review of modern ideas on the vexed question of the origin of petroleum.

Part II, dealing with manufacture, includes sections on distillation and refining. The section on distillation and heat treatment (30 pp.) includes steam, vacuum and combined distillation, and distillation in inert gases. The treatment is from a scientific, rather than from a technical point of view. A new section includes modern advances in the production of motor spirit, with particular reference to liquid- and vapour-phase cracking, and to hydrogenation. The refining of oils with sulphuric acid is dealt with at considerable length (40 pp.), and includes all the latest important data collected from researches in this difficult field. Alternative methods of refining are also dealt with fully, and include processes involving the use of sodium plumbite, hypochlorite, selective solubility and sulphur dioxide.

The final part, Part III, deals with the properties of motor spirit, illuminating and lubricating oils, paraffin wax and vaselines. The section on motor spirits includes a *résumé* of modern theories upon the cause of detonation in the internal combustion engine.

The whole book is concerned with the scientific facts and principles underlying petroleum technology rather than with the technical or commercial aspects involving the preparation of petroleum products for the market. It is of particular interest, therefore, to the technical man dealing with petroleum technology, but should also have a definite appeal to the commercial man, as explaining fully the underlying principles in the preparation of petroleum for the market.

Mr. Harold Moore is to be complimented on having brought this work so thoroughly up to date.

The book is well printed and is presented in a clear and well-arranged form.

J. G. KING

AUSGEWÄHLTE METHODEN FÜR SCHIEDSANALYSEN UND KONTRADIKTORISCHEN ARBEITEN BEI DER UNTERSUCHUNG VON ERZEN, METALLEN UND SONSTIGEN HÜTTENPRODUKTEN. MITTEILUNGEN DES CHEMIKERFACHAUSSCHUSSES DER GESELLSCHAFT DEUTSCHER METALLHÜTTEN- UND BERGLEUTE E.V., BERLIN. Pp. 457. 2 Auflage. Berlin: Gesellschaft Deutscher Metallhütten- und Bergleute, e.V. 1931.

In 1920, a chemical committee was formed by the Gesellschaft Deutscher

Metallhütten- und Bergleute (the German society dealing with metalliferous mining and smelting) to get together a collection of methods which could be recommended for the referee analysis of materials coming within the sphere of the Society's interests. The present committee is composed of some fifty members from various metallurgical and manufacturing concerns, railways, etc., and includes a number of well-known University workers. The work of the committee appeared in 1924–6 in the form of two volumes of methods, which, in the present (2nd) edition, are collected together, with certain additions, in one volume.

The book contains 21 chapters, the first (2 pp.) dealing with generalities in connection with referee analysis, and the succeeding ones each devoted to an individual metal (or substance) or group of metals as follows: aluminium, antimony, arsenic, beryllium, lead, cerium, noble metals, cadmium, carborundum, cobalt, corundum, copper, magnesium, nickel, mercury, selenium and tellurium, bismuth, zinc, tin, "alloy-steel" metals (chromium, molybdenum, vanadium, tungsten). Each chapter has been prepared by a member of the committee having special experience of the matter dealt with, and has been approved by a small sub-committee. These chapters give plain, straightforward descriptions of the main methods for the determination of the element in question, its essential separations from other elements, and methods for its determination in the ores, alloys, etc., which are most likely to be met with in practice by the analyst.

The methods appear, on the whole, to be well-chosen and sound, and up-to-date as judged by the references to Continental literature. Recent English work is not quite so entirely neglected as is often the case in a German book; thus, it is gratifying to note that one example of it is recommended, *viz.* the internal electrolysis method for bismuth in lead recently published in the ANALYST (H. J. S. Sand, ANALYST, 1930, **55**, 309; E. M. Collin, *id.*, 312), and a reference is made to T. B. Smith's outstanding book, *Analytical Processes* (1929). It would, however, have been possible to improve the book in some directions by the inclusion of more of the advances made during the last few years in laboratories in this country and America. A case in point is the method given (p. 366) for determining antimony in commercial tin, which is as given in the first edition, although this was criticised, on the grounds of probable slight loss of stibine during the solution of the tin in hydrochloric acid, by the reviewer (ANALYST, 1928, **53**, 374).

Considering the wide field covered, the book is moderate in size, and the authors, by adopting a concise style which makes the text easy to follow, have been successful in describing a very large number of methods without sacrifice of essential details. The hope expressed in the preface, that the book might gain many friends, is certain to be realised.

S. G. CLARKE

ANALYTICAL CHEMISTRY. Vol. I. QUALITATIVE ANALYSIS, BASED ON THE GERMAN TEXT OF F. P. TREADWELL. Translated and Revised by WILLIAM T. HALL. Eighth English Edition. Pp. xi+640. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. Price 28s. 6d.

That a new edition of this well-known text-book has been called for only two years after the publication of the seventh edition testifies to its wide popularity among English-speaking teachers and students of advanced qualitative analysis.

The last edition suffered from the presence of a large number of printer's errors, and contained several sections which did not fully represent the state of our knowledge of the particular subject at the time of writing. Practically all the errors have been corrected, and the weak parts of the book have been re-written. In his work the author has had the able co-operation of Dr. W. R. Schoeller, who has, among other things, replaced the old sections on tantalum and niobium with new material representing the latest advances made in the qualitative analysis of these troublesome elements.

The only important corrections omitted are in the periodic table of the elements (p. 72), where a tangle in arranging the rare-earth and platinum groups seems to have occurred. A minor criticism might be made of the middle paragraph on p. 500, which describes the separation of caesium from rubidium and potassium by precipitation as chloroantimonite; as this method has already been given at the top of the page, as well as on p. 498, the paragraph is redundant.

A new feature of this edition is a syllabus of the course of instruction in qualitative analysis, as given at the Massachusetts Institute of Technology; this section, which extends to over 26 pages at the end of the book, includes laboratory directions, lecture topics, and a series of well-selected questions suitable for class exercises at the end of a lecture, and is designed to show the utility of the book as a laboratory manual for home study and for reference purposes.

As it now stands, the book is undoubtedly one of the best English works on qualitative analysis. A. R. POWELL

SULPHUR BACTERIA. By D. ELLIS, D.Sc., F.R.S.E. Pp. ix+261, with 66 illustrations. London: Longmans, Green & Co. 1932. Price 21s.

This volume, with its cover appropriately enclosed in a paper of true sulphur yellow, is a monograph on the sulphur-producing bacteria whose habitats are the malodorous muds containing the sulphides of hydrogen and other elements occurring in ponds, rivers and seas in many parts of the world.

The text comprises an extensive summary of our present knowledge of these interesting, but in many ways puzzling, organisms, and is, perhaps, the first attempt to provide a *résumé* of many diverse and scattered investigations conducted during the past century. The most outstanding characteristic of these bacteria is the property they exhibit of liberating a solid element in the free state from at least one of its compounds, but there are many points in their life history which more or less differentiate them from the commoner and better-known organisms. The contents of the volume include the production of hydrogen sulphide in nature and its assimilation by sulphur bacteria; the metabolism, culture, classification and description of the many species of these organisms; the intimate structure of the cell; irritability, chemiotactic phenomena and phylogeny of the sulphur bacteria, and the colouring matter produced by the various species. In addition to the usual general index, one of authors' names and another dealing with the organisms described are provided, together with a comprehensive bibliography, each of which appears to be complete and of a high order of accuracy. The text is by no means a mere abstract of the results obtained by other workers, for the long experience of the author in investigating these organisms, extending over a period of at least twenty-one years, has enabled him to interpolate many valuable and erudite criticisms, besides offering suggestions which are likely to prove invaluable to future workers. The thoroughness with which the subject-matter has been treated is indicated by the sections on the physical chemistry of hydrogen sulphide in aqueous solution; the spectrophotometric investigation of the colouring matters produced by the sulphur bacteria, and the mechanics of ciliary movement. In spite of the numerous workers who have examined many of the species of these organisms, but little definite knowledge has been acquired about the larger number of them, and any investigator attracted by the subject would find an almost unlimited field open to him.

The text throughout is lucid and readable, and the author's sound statements and criticisms are not only of value in connection with the organisms forming the subject of the book, but are of wide application and will enable the reader to avoid many of the pitfalls incident to the study of general bacteriology. As in other branches of this subject, the question of classification is a thorny one, and, after commenting on the systems adopted by Winogradsky, Molisch, Jensen, and other investigators, the author proposes a new one, which appears to be a great advance on those described in the earlier literature.

The book, as a whole, is an admirable production, the typescript being legible and almost free from error; the illustrations, both diagrams and photomicrographs, are clear and well selected, and the binding is well done. There is little meriting adverse criticism; the only items deserving such comment are a reference to "ferrolactate," the formula of which is not given, on p. 24; the substitution of "nef" for "not" on p. 87, and the phrase "highly refractive *drops* of calcium carbonate" on p. 133. The author has carried out what must have been a tedious piece of work in a very satisfactory manner, and has produced a volume well worth the attention of all bacteriologists. T. J. WARD

BREEDING AND CARE OF THE ALBINO RAT FOR RESEARCH PURPOSES. By MILTON N. GREENMAN and F. LOUISE DUHRING. Second Edition. Pp. 121, 18 figures, 11 charts. Philadelphia: Wistar Institute of Anatomy and Biology. 1931. $3.00.

Twenty years ago the use of the albino rat in physiology was confined to a relatively small number of academic investigators. The first edition of this book appeared in 1923, and was in some respects a propagandist venture, although Donaldson's monograph, "The Rat," had preceded it by eight years. For Donaldson the rat was an end in itself, and his statistical survey of the animal's anatomy and physiology, revised and enlarged in 1924, remains a classic.

During the last decade or so, however, the whole position has changed entirely. The rat has ceased to be a mere qualitative instrument for specialised physiologists, and has become a biochemical reagent essential to many branches of bio-assay, more particularly in nutrition and vitamin studies, and to a less extent in endocrinology. If there is any one strain of rat that more than another deserves the qualification "A.R." it is surely the Wistar rat, as witness the increasing number of authors who are content—and rightly—to remark, under the head of "Experimental Methods," simply "albino rats of the Wistar strain were used throughout."

Part of the reason for the steady replacement of mixed and nondescript strains by the Philadelphian breed is to be found in this book. The description of the methods taken to rear a healthy (which means a clean) and a cheerful (which means a healthy) stock should interest even the reader who is not himself directly concerned with the problem. The varied daily menus served at the Wistar Institute secure to the animals a reserve of minerals and vitamins so high that their first generation offspring are, as a matter of fact, useless for deficiency experiments! The anti-infective measures practised are such as might give many a hospital governor food for thought. And the musical entertainment advocated might give the frequenters of British sea-side boarding houses legitimate cause for jealousy.

If the conditions at the Wistar Institute itself are so exceptional as to warrant the description "de luxe," there is a very good reason for it, even though few ordinary laboratories can, or indeed should, attempt to copy them. The Institute has established itself as a world centre for the distribution of A.R. rats. Through subsidiary breeding centres, such as the reviewer's laboratory, the offspring of Wistar Institute ancestors have gone to New Zealand, Buenos Aires, Bombay, Paris, Oslo, Berlin, and numerous other places, and to nearly every university in Great Britain, by rail, road, sea, and air. They have become an essential part of the equipment of many academic, state and industrial laboratories. The stock at Philadelphia must not fail; with the methods advocated and practised by Drs. Greenman and Duhring, it cannot fail.

For those who have no need to take such extreme methods for breeding and care of their animals, there yet remain, in this invaluable book, innumerable hints and suggestions capable of application in humbler animal departments. The chapters on breeding and on diseases and the reference tables are enough to make the book indispensable.

It would, however, be a mistake to suppose that it has been detailed attention to environment, including diet, that has by itself given us the A.R. rat. Something more fundamental was needed, and it is, perhaps, for their insistence on the part played by inbreeding in producing a stock asymptotic to "pure"—a stock that tends continuously to become homozygotic for all Mendelian factors, except in so far as mutations may counteract the tendency—that the workers at Philadelphia have greatest claim on our gratitude. The scientific evidence for this view is to be found in the publications of the Wistar Institute workers themselves—particularly in Dr. Helen Dean King's monograph on "Inbreeding," and in the well-known volume by East and Jones. But the matter can be put fairly simply.

In scientific experiments every reduction in the number of independent variables increases control and accuracy. When animals are used as analytical reagents their genetic "make-up" is an uncontrolled variable, unless animals of identical genetic "make-up" can be compared. The nearest approach we can get to this condition is by using animals as closely inbred as possible, for, the larger the number of ancestors two animals have in common, the more closely alike will they be. A colony of animals bred exclusively by brother-sister mating will, other things being equal, tend to uniformity.

The proof of the homozygosis is in the assay. Winton has shown that intensely inbred animals give, in certain toxicological work, results ten times as certain as an equal number of animals from a mixed stock. The Wistar Institute started its "Tyler Strain" from a pair of animals. In the reviewer's laboratory there are to-day animals removed from these ancestors by some 40 generations, and brother–sister matings have been practised for at least 30 of them. The stock to-day is as fertile and viable as it has ever been, for the bad characteristics thrown up by inbreeding were eliminated at the Wistar Institute during the first dozen or so generations. For later workers the task has been made relatively easy by the foresight, skill and care of Drs. Greenman and Duhring and their colleagues.

A. L. BACHARACH

ASSOCIATION THEORY OF SOLUTION AND INADEQUACY OF DISSOCIATION THEORY. JITENDRA NATH RAKSHIT. Pp. 298. Calcutta: S. C. Auddy & Co. 1930.

This book is written by the Opium Chemist to the Government of India. The author has carried out a number of investigations into the contractions which occur on the dissolution of solids, most of the work being described in the German literature, and in this book he discusses the phenomenon of solution in connection with the properties of specific gravity, contraction effects, surface tension, viscosity, osmotic pressure, thermal effects, optical properties and electrical effects. The views of the author are unorthodox, and he finds little use for the concept of ionic dissociation as an explanation of the deviations from the simple law of mixture usually found in the properties of solutions. As an alternative, an association theory of solution is proposed, it being supposed that a solute can form compounds with a solvent in any proportion. "When a solute dissolves in a solvent all the molecules of both combine with each other in proportion to their dilution, and when the solvent molecules are increased or decreased corresponding association of solvent and solute takes place uniformly. . . . The process . . . is reversible at all conditions." As I understand this theory, there are no free solvent molecules in a solution, but each is bound to a solute molecule. Moreover, "the associated molecules of the solute and the solvent need not bear similarity to those of either component in respect of either chemical, electrical, optical, osmotic, etc., properties." A hypothesis as broad and flexible as this will obviously explain the facts of solution, even if it makes it a very difficult task to correlate the properties of a solution with those of its components, but it is a different matter to substantiate the hypothesis. The author pursues his argument with enthusiasm and vigour, but I closed the book without being convinced of the soundness of his case.

It is admitted in the preface that "it seemed suitable to write this book in English. It would have been happy if I had more control over the language. Readers may have an unavoidable additional inconvenience on account of the book being written in a language foreign to me." While this explains adequately why the argument at times becomes very difficult to follow, it is hardly an excuse for the large number of errors which could have been detected by a more rigorous proof-reading.

R. A. ROBINSON

NOVEMBER, 1932 Vol. LVII., No. 680

P. INST AGR. RES.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Extraordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, October 5th, the President, Mr. F. W. F. Arnaud, being in the chair. Special Resolutions were passed for the alteration of certain of the Articles of Association of the Society.[*]

This was followed by an Ordinary Meeting, at which Certificates were read for the first time in favour of Lionel James Dent, B.Sc., and Leonard Arthur Haddock, B.Sc., A.I.C.

Certificates were read for the second time in favour of Arthur Littlewood, M.A., A.I.C., and John Henry Weber, B.Sc., A.I.C.

The following were elected Members of the Society:—Charles Carr Marginson, B.Sc., A.I.C., Ph.C., Wilfred Mather, A.M.C.T., F.I.C., Alec Duncan Mitchell, D.Sc., F.I.C., and M. Niyogi, M.Sc.

Mr. E. Hinks, B.Sc., F.I.C., gave an account of the work embodied in the Third Report of the Milk Products Sub-Committee, on The Analysis of Condensed Milk in which the Sucrose has altered during Storage, and the following papers were read and discussed:—"A New Copper Reagent for Sugar Determinations," by E. B. Hughes, M.Sc., F.I.C.; and "A Colorimetric Method for the Determination of Chloroform," by W. G. Moffitt, Ph.D., A.I.C.

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[*] That Article 6 of the Articles of Association of the Society be deleted and the following substituted therefor:

6. Every candidate for membership of the Society shall be not less than 21 years of age and shall be or have been engaged in analytical, consulting or professional chemistry. Each candidate for election shall be proposed by three members of the Society who shall provide written testimony of their personal knowledge as to his scientific and professional fitness. If the Council in their discretion think fit such testimony may be dispensed with in the case of a candidate not residing in the United Kingdom. Every application shall be placed before the Council and the Council shall have the power in their absolute discretion to suspend or reject any application. Each application passed by the Council shall be read at the next Ordinary Meeting of the Society and shall be circulated to members prior to the next following meeting so that the voting which shall be by ballot may take place at that meeting. It shall be competent for members who are unable to be present to send their ballot papers through the post. The candidate shall be elected if not less than three-fourths of the votes recorded are in favour provided also that the total number of votes recorded be not less than 20. If less than 20 votes are recorded the candidate shall come up again for election at the next Ordinary Meeting of the Society.

6a. Any member may at any time by notice in writing to the Secretaries resign his membership but such resignation shall not free him from liability to pay any annual subscription or money which may be due from him to the Society.

That in Article 34, line 1, "Article 39" be deleted and "Article 36(b)" be substituted therefor.

That in Article 36, line 1, "(a)" be inserted after "36," and that at the end of the Article the following be added: (b) Notwithstanding the provisions of Articles 34, 35 and 36(a) the Officers and Council shall include the Chairman for the time being of the North of England Section of the Society as an additional Vice-President and the Secretary for the time being of that Section as an additional Member of Council.

NORTH OF ENGLAND SECTION

A MEETING of the Section was held on October 15th, in Manchester. The Chairman (Mr. J. Evans) presided over an attendance of thirty-four.

The following papers were read and discussed:—"The Quantitative Separation of Aluminium from Iron," by J. Haslam, M.Sc., F.I.C.; "An Improved Micro-apparatus for the Determination of Molecular Weights," by A. F. Colson, B.Sc., A.I.C.; "The Spontaneous Combustion of Hay," by F. Robertson Dodd, F.I.C.; "The Examination of a Proposed New Method for the Identification and Estimation of Oils and Fats," by J. R. Stubbs, M.Sc., F.I.C., and Arnold Lees, F.I.C.; and "The Freezing-point of Pasteurised and Sterilised Milks," by G. D. Elsdon, B.Sc., F.I.C., and J. R. Stubbs, M.Sc., F.I.C.

Deaths

THE Society has suffered a great loss by the death, on October 17th, of Mr. A. Chaston Chapman, Past-President. An obituary notice will be published later.

We also regret to have to record the death of Mr. W. Hepworth-Collins, who had been a member of the Society since 1897.

The Estimation of Hormones

BY K. CULHANE, B.SC., A.I.C., AND S. W. F. UNDERHILL, M.A., B.M., B.CH.

(*Read at the Meeting, April* 6, 1932)

MANY glands of the body secrete into the blood-stream substances which exert a powerful drug-like action and serve to correlate the functions of different organs and tissues. The earliest step in the investigation of the functions of these glands of internal secretion was the observation of the effects caused by removal of the glands from animals, or their grafting into a different position in the body. The study of the phenomena produced by the injection of extracts has been a later development. Berthold, in 1849, found that the implantation of testicular grafts into capons restored the appearance of the birds to that of normal cocks, and concluded that the testes must pass into the blood some substance which affects the whole organism. Some ten years later Claude Bernard formulated the idea of internal secretion, but gave it wider significance than the term connotes to-day. A quarter of a century later the Swiss surgeons, J. L. and A. Reverdin, and Th. Kocher found that removal of the thyroid gland in patients suffering from goitre led to the onset of a condition which had already been recognised as a clinical entity termed myxoedema. A few years later Minkowski and von Mehring showed that removal of the pancreas from animals led to the development of diabetes mellitus, and Brown-Séquard described the effects upon himself of the administration of testicular extracts.

The first demonstration that it was possible to obtain active extracts of the glands of internal secretion occurred in 1894, when Oliver and Schäfer injected simple extracts of a number of them intravenously into animals, and observed the effects produced upon the blood pressure. They found that extracts of the suprarenal or pituitary glands caused a rise in blood pressure, whilst a fall was produced by extracts of all the others investigated. Ten years later Bayliss and Starling reported the discovery of secretin, and proposed the name "hormone" for the active principle of the glands of internal secretion. Secretin is, perhaps, the simplest example of a hormone. The acid which passes from the stomach into the duodenum with the semi-digested food is absorbed by the cells lining this part of the small intestine, and converts the precursor of secretin in these cells into the active principle itself. The hormone is then absorbed into the blood-stream and carried round the body until it reaches the pancreas, the acinous cells of which are stimulated to pour out their secretion into the ducts of the gland, whence it finds its way into the upper part of the duodenum. Secretin thus has the single function of stimulating the cells of the pancreas, and does not act on other cells in the body (except possibly those of the liver).

Other hormones have more complicated functions, acting upon a variety of tissues. Thus adrenaline, the active principle of the medulla of the suprarenal glands, has the same effects upon the tissues as stimulation of the sympathetic nerves proceeding to them. Although removal of this part of the suprarenal gland has not been shown to have any very striking result, yet stimulation of the secretion of adrenaline or its administration is productive of very profound effects. Adrenaline, in fact, is secreted at times of stress or emotion, and is responsible for the rapid heart beat, the dry mouth, the cold and clammy skin observed at moments of extreme shock. The familiar response of a cat to the approach of a strange dog is conditioned by the outpouring of an extra amount of adrenaline from its own glands.

The powerful effects which the active principles of these glands exert upon the bodily economy is evinced by the observation of the results of their under- or over-production in human beings. Hypo-secretion of insulin, the active principle of the internal secretion of the pancreas, leads to the development of the disease known as diabetes mellitus. Again, hypo-secretion of thyroxine, the active principle of the thyroid gland, is responsible for the condition known as cretinism in the child or myxoedema in the adult. A cretin shows under-development of both mind and body; a myxoedematous patient shows dulling of the mental faculties, lethargy, and a peculiar oedematous condition of the skin. Hyper-secretion of the thyroid gland, on the other hand, is the cause of Graves' disease, in which the patient suffers from palpitation, nervousness, flushing, wasting, and protrusion of the eye-balls; whilst over-production of the secretion of the anterior lobe of the pituitary gland results in gigantism if it occurs before growth has ceased, or in acromegaly in the adult.

Enough has been said to show the profound effects which these compounds exert upon both mind and body. It might be expected, therefore, that extracts of these glands would be powerful therapeutic agents, and it has, in fact, gradually become apparent that the body itself is the best factory for a number of therapeutic substances.

The hormones have been used to replace the natural secretion when that is deficient, and also as drugs to modify the function of the body in some desired manner. The use of insulin in diabetes mellitus, of thyroxine in myxoedema or cretinism, of pituitary posterior lobe extract in diabetes insipidus, and of extracts of the cortex of the suprarenal gland in Addison's disease, are all examples of this replacement or substitution therapy. On the other hand, adrenaline finds its chief clinical value in asthma, and as a constituent of solutions used in local anaesthesia. Pituitary posterior lobe extract is widely used as a uterine stimulant at the end of labour, and to raise the blood pressure in conditions of shock.

As with all drugs, there is a limiting dose which cannot be safely exceeded. It is, therefore, essential for the physician to employ an accurate dosage, and this necessitates special methods of test when the compound used cannot be obtained in a chemically pure condition. An over-dosage of insulin, for instance, may produce most alarming symptoms. As the blood sugar falls, the patient shows signs of uneasiness with palpitation and sweating; mental distress and disorientation are common, and may be followed by coma which can be distinguished from diabetic coma only by determining the sugar in the blood. Convulsions, as a result of this over-dosage, are rare in human beings, although they are a frequent symptom of the toxic action of insulin in animals.

Although active extracts have been obtained from the majority of glands possessing an internal secretion, in only three or four cases have pure crystalline compounds been isolated, and in only two, namely, those of adrenaline and thyroxine, has the isolation been followed by a determination of the chemical constitution. Little is as yet known of the chemical constitution of insulin, although it can now be crystallised, or of the active principles of the pituitary and the parathyroid glands. For advances in this field it is necessary to have available suitable physiological and chemical methods of assay. Insulin would never have reached its present position in therapeutics without a simple method of physiological assay, and a simple method of estimating the sugar in the blood, nor would oestrin, one of the active principles of the secretion of the ovary, have been isolated in a pure crystalline condition, if a simple, accurate, and rapid method of physiological assay had not been available.

As long ago as 1908 Zuelzer obtained extracts of pancreatic glands which were active in diabetic subjects. Knowlton and Starling, a few years later, obtained an extract which restored to normal the decreased rate of disappearance of sugar in the heart of a diabetic animal. Other workers obtained extracts which were frequently potent, but, without a suitable method of assay, found it impossible to purify the hormone and separate it from other toxic compounds. Soon after Banting and Best commenced their work in 1921 they found that injections of their extracts resulted in the lowering of the blood-sugar of normal rabbits. Thus they had at their disposal a simple test, since the rabbit is a convenient laboratory animal from which small amounts of blood can rapidly be withdrawn without harm, and methods of determining the sugar in the blood had by then been so far developed that the assay could be carried out with the highest accuracy on very small quantities.

In 1923 Allen and Doisy found that the rat showed a vaginal reaction similar to that described by Stockard and Papanicolaou in the guinea-pig: the cells obtained by rubbing a spatula on the vaginal walls varied according to the oestrous condition of the animal. The isolation of oestrin was made possible by this discovery, since the reaction, as employed with the rat or mouse, is capable of a quantitative expression when a number of animals are used, and has enabled investigators to follow the activity in all the processes of purification and isolation. It is of interest to note that the clinical indications of oestrin are still obscure. The same is true of the hormone of the testis which A. Butenandt (*Z. angew. Chem.*, **1931, 44,** 905) has recently claimed to have isolated in pure crystalline form. The great differences in the reproductive processes of different species, their cyclic character, and the fact that the same gland may secrete a succession of hormones, are at the base of our lack of knowledge of the clinical value of these preparations.

Although extracts of the parathyroid glands have a considerable therapeutic value, little is known of the chemical properties of the hormone itself. It may be surmised that this is due to the fact that a simple method of physiological assay has not yet been found, nor is there available a satisfactory micro-method for the estimation of calcium in blood. Small laboratory rodents are resistant to parathyroid gland extracts, and it is necessary to carry out the tests upon dogs.

Thyroxine is more stable than the other hormones, and is characterised by its content of iodine. It was, therefore, possible to follow its isolation from the thyroid gland by chemical means, the physiological test being used only to confirm the activity of the isolated product.

Extracts of the glands of internal secretion are of great and increasing importance in therapeutics, and their commercial production has, so far, preceded the definition of their chemical properties, so that they present great difficulties to the analyst; yet, in view of their potent action and the important uses to which they are put, it is essential that adequate tests should be carried out before their issue for use by physicians.

At present, insulin, extract of the posterior lobe of the pituitary gland, adrenaline, and thyroxine, find widest use in medicine. No chemical methods of estimation or even identification of insulin and pituitary posterior lobe extract are yet available. They can be identified and estimated only by physiological tests. Both are scheduled preparations in the Regulations made under the Therapeutic Substances Act, 1925 (Statutory Rules and Orders, 1931, No. 633), and physiological methods of assay have been specified in the British Pharmacopoeia, 1932.

Adrenaline is a well-defined chemical compound which may be prepared either from suprarenal glands or synthetically. Synthetic adrenaline may be contaminated with small amounts of impurities which have not so far been detected chemically, although they have a considerable influence upon the physiological activity. The physiological test, which is simple and accurate, is therefore more reliable than chemical or physical methods of estimation.

In the case of thyroxine, determinations of the percentage of iodine and of the melting point offer sufficient indications of its purity, and are much simpler than physiological tests. In therapeutics, however, thyroxine is most commonly administered in the form of dried thyroid gland. In this preparation it is present as laevo-thyroxine in peptide combination. The laevo compound is more active physiologically than the synthetic racemic substance, and the activity is still further modified when it is present as a peptide, partly owing to its greater solubility. Determination of thyroxine iodine, therefore, may not prove a completely reliable index of the potency of such preparations, but physiological tests are difficult to carry out, and do not show a high degree of accuracy, so that, for practical purposes, the chemical method is the more satisfactory.

Extracts of the male and female reproductive glands, and of the anterior lobe of the pituitary gland, have as yet no definite clinical indications. Extracts of the parathyroid glands and of the cortex of the suprarenals are of definite clinical value, but no active principle has yet been isolated; except in the case of oestrin the methods of physiological assay of all these hormones are only very roughly quantitative.

In the following account we confine ourselves to a description of the assay of insulin, pituitary posterior lobe extract, and adrenaline.

PRINCIPLES OF BIOLOGICAL TESTS.—When the same dose of a drug is injected into a series of animals of the same species, it is usually found that the effects produced on the different animals differ in degree. Thus a dose can be found which will kill some of the animals, but not others, or which will have a greater physiological effect in some animals than in others, for example, in reducing the blood sugar or raising the blood pressure. At one time physiologists were inclined to overlook these individual variations, and, by the use of a few animals given rather widely spaced doses, attempted to determine the minimum dose of the compound under examination which would have an effect in the particular group of animals used. Hence arose the term "minimum lethal dose" or M.L.D. The figure obtained for the M.L.D., however, may vary according to the variations in the response of different animals under the same conditions. Even if the average lethal dose is taken instead of the minimum lethal dose, there is no guarantee that this figure will be the same when determined on different stocks of animals by different investigators. Owing to the many factors affecting animal reactions it is possible to obtain comparable results in different laboratories and in different countries only when the sample under examination is assayed in terms of a suitable standard. The results of the assay are then expressed in terms of this standard instead of in terms of the animal reaction. An example of the use of the standard will perhaps make this clear. If a given dose of insulin is injected subcutaneously into rabbits, the blood sugar may fall after a couple of hours to a level of 45–80 mgrms. per 100 c.c. If 45 mgrms. per 100 c.c. is taken as the unit of the reaction, it is clear that a larger dose of insulin will be required in the case of the more resistant animals than in the case of the more sensitive to reduce the blood sugar to this level. As it is not possible to obtain animals of uniform sensitiveness, a dose which will produce an average fall to 45 mgrms. per 100 c.c. on one occasion or on one stock may on another occasion on another stock only reduce the blood sugar to 80 mgrms. per 100 c.c., in which case the potency of the preparation will be considered to be only one-half its previous value, although actually it is of exactly the same activity. If, instead of the actual level of the blood sugar in a series of animals being taken as the unit of reaction, the effect of the test solution is compared with the effect produced by the standard injected at the same time into a similar series, the activity of the former can be expressed as a percentage of the activity of the standard, since the variation in the sensitiveness of the different animals under controlled conditions is likely to be the same. The effect of the variability of the animals can be reduced to a minimum only by using fairly large groups of a uniform stock.

The preparation of suitable standards of reference is a matter of international importance, and has been undertaken by the Health Organisation of the League of Nations. Standards have been issued for insulin, pituitary posterior lobe extract, and adrenaline, as well as for a number of other biological products and drugs which cannot yet be submitted to a chemical or physical test. Other standards will be adopted and issued from time to time by the Permanent Commission on Standardisation of Sera, Serological Reactions and Biological Products, as our knowledge of the physiology and clinical value of this group of substances warrants. The same standard of reference is now used in all countries to control the potency of these preparations so that their activity wherever obtained, when made to a definite potency, should be exactly the same. In Great Britain the Medical Research Council maintains and distributes suitable standards for these biological products (*cf.* ANALYST, 1932, 173). The international adoption of these standards marks a great advance when it is remembered that most of these substances were unknown a quarter of a century ago.

We have used above the term "unit." In the early tests of any of these preparations it was found convenient to select a certain response which was somewhat less than the maximum obtainable as a unit of activity. The next step was the setting-aside of a preparation of the compound as a standard, and its definition in terms of units of activity. Thereafter, it is not necessary, as shown above, for all the animals in a group to show the same response. A given number of units is administered to all the animals of a group, and their average response is determined. The average response of another similar group to a dose of the sample under examination is also found. By adjustment of the dose given it is possible to obtain the same average response in the two groups. The dose of the sample then contains the same number of units as the dose of the standard.

The methods of biological assay to which we refer below illustrate the application of these principles in the differing circumstances of each test. The simplest case is when doses of sample and standard can be administered alternately to the same animal preparation, as in the assay of the oxytocic potency of pituitary posterior lobe extract, or the pressor potency of adrenaline. In the case of insulin, in the rabbit test, the same animal is given at different times a dose of the standard and a dose of the sample; in the mouse test, different animals are injected, some with the standard, others with the sample, at the same time.

INSULIN

Although insulin can be crystallised and different preparations have the same potency, little is known about its chemical constitution. No chemical or physical tests of identification or estimation are yet available, so that reliance must be placed entirely upon physiological methods. Chemical and physical methods of estimation have been put forward, but none has been found sufficiently specific. Recently, W. Graubner (*Z. ges. exp. Med.*, 1928, **63**, 527), and W. Kuhn, H. Eyer, and K. Freudenberg (*Z. physiol. Chem.*, 1931, **202**, 97) have found that the ultra-violet spectrum of insulin shows a point of maximum absorption at a wave-length of about 272·5$\mu\mu$. This, however, is also shown by other proteins or mixtures of amino acids such as tyrosine and cystine. F. K. Crews has examined the spectra of a number of samples of insulin of varying potency. Although there is a tendency for those of very low activity to show less absorption, and those of high potency a greater absorption, there is a range between potencies of about 5 to 20 units per mgrm. in which the absorption remains almost constant (unpublished observations).

Methods of physiological assay are based on the reduction of the blood sugar produced by an injection of insulin. Either this reduction is directly measured, or its effect on the animal, namely, the appearance of convulsions, is taken as the criterion. In our experience the method in which rabbits are used, described by Marks (*The Biological Standardisation of Insulin, Publications of the League of Nations*, III, Health, 1926, III, 7 Ch., 398, p. 57), and that in which mice are used, described by Trevan and Boock (*ibid.*, p. 47), are the most suitable. For all accurate assays it is essential to employ a method permitting the direct comparison of the sample with the standard of reference. The present standard is the International Standard adopted by the Health Organisation of the League of Nations (*ibid.*, p. 7), which is defined as containing 8 units per mgrm. For use it is convenient to dissolve it at about 20 units per c.c. in acidified water (p_H 4) containing 0·3 per cent. of cresol. This solution is perfectly stable. It is our practice, however, to renew it every two months. Further dilutions are made from this stock solution as required.

QUALITATIVE TESTS.—As a preliminary to a more accurate assay, time and rabbits can be saved if one has some knowledge of the hypoglycaemic potency of the sample to be tested. For this purpose two or three rabbits are starved for 22 hours and their resting blood sugars are then determined. A dose of the sample is injected subcutaneously, and the blood sugar is determined hourly until the minimum is reached. 0·25 unit per kilo. usually gives a minimum at the first hour, 0·5 unit one at the second, and 0·75 unit one at the third hour. By noting the position of the minimum it can thus be seen whether the dose given is of the order of half a unit, or greater or less, information which is invaluable for the selection of a suitable dose for the quantitative test.

QUANTITATIVE ASSAY

(1) THE RABBIT TEST.—We have found it essential to use carefully selected animals, and to keep the stock under conditions as uniform as possible. Young healthy rabbits of 1600–3000 grms. in weight, with large ears, are the most suitable. They should be kept at a constant environmental temperature and on a constant diet, *e.g.* oats, hay, and cabbage. As an aid to their selection all animals should receive a subcutaneous injection of 0·5 unit per kilo. of the standard preparation, and any which develop convulsions should be discarded. It is also advisable to discard them after they have been in use for more than

two or three months, if they habitually give figures for the percentage blood sugar reduction (as defined below) of less than 15 or more than 45, and if at any time they have received doses varying greatly from 0·5 unit per kilo. Pregnant females or animals which have had litters should not be used. Further details on the selection of rabbits are given by K. Culhane (*Quart. J. Pharm.*, **1928**, **1**, 517).

The test is performed in two parts, the first on one day, and the second three or four days later.

First Part of Test.—An even number of rabbits, in any case not less than ten, is selected, and all food withdrawn from their cages 22 hours before the test. On the morning of the test the animals are weighed and divided into two groups, in such a manner that for each animal of a given weight in one group there is one of approximately corresponding weight in the other group, so that both the total weights and the distribution of individual weights in the two groups are as far as possible the same. A sample of blood is withdrawn from the ear vein of each rabbit, 2–5 mgrms. of potassium oxalate being added to each c.c. to prevent clotting, and the percentage of blood sugar determined. We have found it convenient to use a modification of the Folin–Wu method, in which the sugar in the protein-free filtrate is estimated colorimetrically. The method is simple and rapid, and allows one observer to carry out as many as 120 estimations in one day. It is known that the readings of the colorimeter are not quite proportional to the ratio of the sugar content of the test solution to that of the standard solution. To correct for this error we have constructed a curve relating the reading of the colorimeter to the amount of sugar present when the standard is set at 20 mm. The use of this curve considerably increases the accuracy of the method, and is quicker than other means of correction that have been proposed. An accuracy within ± 2–3 mgrms. glucose per 100 c.c. of blood is attained.

Each rabbit in the first group receives a subcutaneous injection of 0·5 unit per kilo. body weight of the standard preparation, and each animal of the second group a dose of the sample under test expected to be equivalent. Both sample and standard are diluted so that each animal is given a volume of 0·25 c.c. per kilo., and all injections are made at regular intervals of three minutes. Samples of blood are withdrawn from the ears of each of the rabbits at the end of the first hour after the injection, and at each of the subsequent four hours. It is convenient to pool the five samples from one rabbit; 0·2 c.c. of blood is, therefore, delivered into a test tube containing 8 c.c. of $N/12$ sulphuric acid, and the mixture is shaken thoroughly at each sampling. After addition of the last sample, 1 c.c. of a 10 per cent. solution of sodium tungstate is added, the solution well shaken, and the estimation of the sugar carried out on the filtrate after removal of the precipitate. No glycolysis occurs over the five hours of the experiment.

The difference between the initial blood sugar and the average blood sugar for the five hours, expressed as a percentage of the initial figure, is referred to as the "percentage blood sugar reduction."

Second Part of the Test.—The same animals are again prepared for test three or four days later by withholding food for the previous 22 hours. The same doses per kilo. are used, but on this occasion the animals which were given the standard preparation on the first day now receive the dose of the sample, whilst those which were given the sample on the first day now receive the dose of the standard. The percentage blood sugar reductions are determined as before.

The sum of the percentage blood sugar reductions of the animals when given the dose of standard, and the corresponding sum when given the dose of the sample are now determined, and the second figure expressed as a percentage of the first. This figure represents the percentage activity of the unknown solution in terms of the solution of the standard preparation.

While the total percentage reduction is roughly proportional to the dose within certain limits, as in all physiological assays it is possible to obtain an accurate determination only when the dose of the sample produces the same effect as the dose of the standard. In this case the assay may be considered accurate to within ± 10 per cent.; frequently a greater accuracy is attained. When the result of the test indicates that the assumed value of the sample differs from the observed value by more than 10 per cent., the test must be repeated, using a dose of the sample per kilo. body weight calculated on the basis of the first test to contain 0·5 unit.

Success in the method depends chiefly on a proper selection of rabbits and of the dose given to them, and upon a rigid adherence to the exact times for taking blood samples.

(2) MOUSE TEST.—An inbred stock should be employed and should be maintained at a constant environmental temperature and on a constant diet, such as brown bread soaked in water, and mixed with canary, millet, hemp, or linseed in rotation, cod-liver oil and chopped cabbage being added once, and dried cheese twice a week. All mice are starved from 5 p.m. on the day preceding test.

At least sixty mice, weighing between 16 and 22 grms. each, are divided into two groups as uniformly as possible. Each mouse of the first group is then given a subcutaneous injection of 0·02 unit of standard, and each of the second group a dose of the sample expected to be equivalent. Both the standard and sample under examination are diluted with water acidified to p_H 4·0, so that the required doses are contained in 0·1 c.c. of solution. Immediately after injection the animals are placed in small ventilated boxes immersed in a specially constructed thermostat at a constant temperature of 37·5° C. Five mice are put into each box, and it is our practice to inject in groups of five, standard and sample in alternate order. The number of convulsions occurring during the ensuing 1½ hours is noted, and the percentage on standard and sample is determined. Animals developing convulsions are immediately given a subcutaneous injection of 0·2 c.c. of 20 per cent. glucose solution. They suffer no ill effects, and can be used again in subsequent tests.

The result of the assay is obtained from a curve relating dose given to percentage developing convulsions. Such a curve is constructed by injecting the standard preparation in varying doses into a large number of mice, and may be kept as a standard of reference. The curve that we use was obtained by injecting about 240 mice for every point.

In calculating the result of a particular test, the dose of standard corresponding with the observed convulsions on the standard is read off on the curve. The ratio between this and the actual unit value of the dose injected gives a factor for the day variation. The dose of standard that would correspond with the number of convulsions given by the sample is next read from the curve, and the result is divided by the day variation factor.

Thus if x and y are the percentage numbers of convulsions observed on the sample and standard respectively, and from the curve, B is the "characteristic" dose of standard to give y per cent. of convulsions, then the ratio $\frac{B}{0{\cdot}02}$ gives the Day Variation Factor, 0·02 unit being the actual dose of standard given.

If A is the dose from the curve corresponding with the x per cent. of convulsions obtained on the sample, the potency is then given by $A \times \frac{0{\cdot}02}{B}$, for the number of units contained in the 0·1 c.c. injected.

The potency of the original solution is calculated from this result by reference to the dilution made.

With the use of such a "characteristic" curve and of thirty mice on the standard preparation and on the sample, the error of the result may be considered to be ±10 per cent., provided that the number of convulsions on the standard is approximately equal to that on the sample. If this is not the case, the test should be repeated, of doses of standard and sample being used which are estimated to produce the same number of convulsions in both groups of mice. The result shows the greatest accuracy when the number of convulsions falls on the straight part of the curve (30–50 per cent.). Tests in which a very high or very low value is obtained should be repeated after adjustment of the dose.

PITUITARY POSTERIOR LOBE EXTRACT

Since it is possible to separate the different activities of this extract, it is necessary to carry out separate tests for each activity. The same International Standard is used for each one; from 0·5 mgrm. of this preparation, 1 unit of specific activity can be obtained. The standard should be kept in a weighing bottle *in vacuo* over phosphorus pentoxide. For the test a small quantity is accurately weighed out into a test-tube, and 0·25 per cent. acetic acid is added, a volume of 1 c.c. being used for each mgrm. of powder taken. The test-tube is plugged with cotton-wool, heated on the boiling water-bath for 3 to 10 minutes, and the extract, which contains 2 units of activity per c.c., is filtered through dry paper.

Pituitary posterior lobe extract is used clinically for its activity in stimulating contraction of the uterus, raising the blood pressure, and inhibiting the secretion of the kidneys. Tests should be carried out for each of these properties. Although we have found that the oxytocic or uterus-stimulating power and the pressor or blood pressure-raising power usually vary together, it is generally considered that they are properties of two different substances which can be separated; the principle which inhibits kidney secretion is the same as, or closely related to, that acting on the blood pressure.

TEST FOR OXYTOCIC POTENCY.—The excised uterus of the virgin guinea-pig is used as test object; the technique of the test is described by J. H. Burn and H. H. Dale (*Reports on Biological Standards*, I, *Pituitary Extracts*, Medical Research

Council: Special Report No. 69, London, 1922). Attention must be directed particularly to the following points:—Guinea-pigs weighing 200–250 grms. are the most suitable. They should have been kept away from contact with males from the time of weaning. The vagina should be closed, indicating that the animal is not in oestrus. It is killed by a blow on the head, and one horn of the uterus, together with the ovary at its upper pole, is carefully dissected out without stretching, the lower end being cut away from the vagina. It is then set up in a bath of warm oxygenated Ringer–Locke solution, the lower end being attached to a fixed hook, and the upper hook passing through the ovary and being attached to a frontal writing lever. The bath, which should contain about 100 c.c. of Ringer–Locke solution, is surrounded by a water-bath maintained at a constant temperature of 37° C. The preparation is left undisturbed for about 20 minutes, during which time it relaxes to a constant level. A suitable uterus should show small irregular contractions. If these are large, it should be discarded and a fresh one obtained. A suitable formula for the Ringer–Locke solution is as follows:—Sodium chloride, 9; potassium chloride, 0·42; calcium chloride, 0·24; magnesium chloride, 0·005; glucose, 1·0; sodium bicarbonate, 0·5 grms.; water (distilled), 1 litre.

It is absolutely essential that the salts and water used should be free from traces of the heavy metals.

The apparatus is so designed that the Ringer–Locke solution can be repeatedly run off and replaced by fresh solution at the same temperature. The lever should be provided with a Bowden cable, such as is used for the shutter release of a camera, to hold it steady during the time the solution is being changed. The lever should be weighted with 0·5 to 1 grm.; the magnification need not be more than two diameters.

In carrying out the test the standard solution should be diluted 100 times. The first dose may be 0·5 c.c. of this dilution, that is, 0·01 unit, but less or more may be required according to the uterus. A dose must be selected which gives a contraction slightly less than the maximum. Alternate doses of the standard and the solution under test are then added to the bath at regular intervals, which may vary in different experiments from 10 to 20 minutes. As soon as the contraction has reached its maximum after each addition, the Ringer–Locke solution is changed twice, to wash away the active principle still remaining in the bath. The object of the test is the determination of a dose of the sample which gives a contraction equal to that produced by the dose of standard. Since the contractions given by the same dose may not always be exactly the same, confirmation of equality is obtained by finding the doses of sample which produce contractions slightly less and slightly greater than that given by the dose of standard. In each case it is essential, for an accurate assay, that two pairs of doses be used for the comparison, since the size of a contraction is frequently influenced by that of the preceding response, especially when the doses given are not exactly equal. It is sometimes advisable to add the doses in the order standard, sample; sample, standard, rather than alternately. When the comparison has been carried out on six pairs of doses in this manner, the result may be considered accurate to within 15 per cent. Frequently a greater accuracy is attainable.

The uterus of the guinea-pig also contracts to histamine, which may be present as an impurity in extracts of the posterior lobe. It can be detected by treating them with *N* sodium hydroxide solution for one hour at room temperature, neutralising to litmus, and re-testing. The oxytocic activity of the pituitary extract is destroyed by this treatment, any remaining stimulant power being due to the presence of histamine. Not more than 5 per cent. of the oxytocic power of the extract tested should be due to the latter, or not more than 0·1 mgrm. of histamine should be present per 10 units of oxytocic activity.

The United States Pharmacopoeia requires the use of this method for the assay of solution of pituitary; the standard, which is prepared from the posterior lobes of the pituitary bodies of cattle by the method of M. I. Smith and W. T. McClosky (*U.S. Public Health Service Hygienic Laboratory, Bulletin No.* 138, Washington, 1924), has since been accepted as the International Standard.

TEST FOR PRESSOR POTENCY.—This may be carried out on the decapitated cat or the anaesthetised atropinised dog. Both methods are described by the Health Organisation of the League of Nations. We have found it convenient to use the decapitated cat. The method of preparation is described by J. H. Burn (*Methods of Biological Assay*, London, 1928, p. 46).

In brief, the animal is anaesthetised with ether, the carotid arteries are tied and the spinal cord is exposed by an incision in the midline of the back of the neck, followed by removal of the arches of the upper cervical vertebrae. The spinal cord is then cut across in the upper cervical region and the brain destroyed by a probe. Preparations are made for injecting the extract into a femoral vein, and for recording the blood pressure in a carotid artery on the kymograph. It is, of course, necessary to supply artificial ventilation of the lungs after the brain has been destroyed.

The object of the assay is the determination of the dose of the preparation under test which produces a rise in blood pressure exactly similar to that given by the selected dose of standard. Doses can be given only at infrequent intervals. L. T. Hogben, W. Schlapp, and A. D. McDonald (*Quart. J. Exp. Physiol.*, 1924, 14, 301) recommend hourly injections, but we have found it possible to give them as frequently as every half-hour. When one dose follows another too quickly the preparation has not recovered from the effects of the earlier dose, so that successive injections of the same dose produce successively smaller rises in blood pressure. Injections may be commenced about an hour after the destruction of the brain, when the blood pressure has reached a constant low level. A suitable dose for injection into a 3–4 kilo. cat is 0·25 unit. The dose of standard should be one which gives about half the possible maximum rise of blood pressure. Alternate doses of the sample under examination and the standard are given with the object of determining the dose of sample which gives the same rise of blood pressure as the dose of standard. The error of the assay may be taken as 20 per cent., but in many cases is not more than 10 per cent.

TEST FOR ANTIDIURETIC POTENCY.—Assays have been carried out on human beings, dogs, mice, and rats. The Health Organisation of the League of Nations recommends the use of the unanaesthetised dog, the normal man, or the patient with diabetes insipidus (E. Knaffl-Lenz, *Publications of the League of Nations*, III, *Health*, 1928, III, 10, Ch. 734, p. 55). The method involving the use of rats described by J. H. Burn (*Quart. J. Pharm.*, 1931, **4**, 517) appears the most suitable. It is based on a method originally described by O. S. Gibbs for use with mice (*J. Pharmacol. Exp. Therap.*, 1930, **40**, 129).

Sixteen rats, weighing 120–140 grms. each, are employed for each test, divided into four groups of four. Males give better results than females. The test is divided into two parts. Food is withdrawn from all the animals from 5 p.m. on the day preceding the test, but water is left in their cages. Each group is placed in a metabolism cage resting on a large funnel, and given warm tap-water by mouth, with the dose of pituitary extract subcutaneously immediately afterwards. Five c.c. of water per 100 grms. body-weight are administered by means of a gum elastic catheter passed through the central hole in a small wooden gag held in the animal's mouth. Two groups are injected with the standard extract, and two with the sample under examination, a suitable dose being 0·006 unit per 100 grms. body-weight. The amount of urine excreted by each group is noted every 15 minutes, and the time taken to reach maximum excretion is thus determined. Two days later the test is repeated after a preliminary fasting period as before, but the two groups which were given the standard are now injected with the sample, and the two which were given the sample are injected with the standard.

The average times to maximum excretion for all four groups on the standard and on the sample are then determined. The relationship between the doses giving these effects is obtained by reference to a curve relating dose to effect. This is obtained in the same way as the mouse insulin curve by experimentation on a large number of animals with doses of standard ranging from 0·002 to 0·016 unit per 100 grms. body-weight, and is kept for reference (see under Physiological Assay of Insulin by the Mouse Convulsion Method for the use of such a curve). The error of the test is not more than 20 per cent.

ADRENALINE

Adrenaline can be determined chemically by a method described by Folin, Cannon, and Denis, depending upon a colour reaction, which is sensitive to 1 in 3 million (*J. Biol. Chem.*, 1913, **13**, 479). It is not, however, absolutely specific. Briefly, the method is as follows:—Two grms. of the sample of suprarenal glands are digested with 15 c.c. of 0·1 *N* hydrochloric acid and 45 c.c. of water for one hour. The mixture is gradually heated to boiling, 5 c.c. of 10 per cent. sodium acetate solution are added, and the mixture is boiled for two minutes. It is then transferred to a 100-c.c. flask and diluted to the mark with water. As much of the solution as is required is filtered or centrifuged. Five c.c. of the clear solution are transferred to a 100-c.c. flask, and 2 c.c. of sodium tungstate reagent are added, followed by 20 c.c. of saturated sodium carbonate solution. The sodium tungstate reagent is prepared by boiling gently for two hours 100 grms. of sodium tungstate, 80 c.c. of 85 per cent. phosphoric acid, and 750 c.c. of water; the solution is made up to one litre when cold. After addition of the sodium carbonate solution, the mixture is shaken, and, after two to three minutes, is made up to volume with water. One c.c. of a freshly-prepared 0·1 per cent.

uric acid solution is put into a second 100-c.c. flask, and 2 c.c. of the reagent and 20 c.c. of saturated sodium carbonate solution are added. After two to three minutes the standard solution is also made up to volume, and the two solutions are compared in the colorimeter; the result is calculated from the known fact that uric acid gives a colour which is identical in kind with, but is only one-third as intense as that given by adrenaline. The results by this method agree well with, on the whole, those obtained by the physiological test.

The optical rotation of a sample of adrenaline should be a good indication of its purity. We have found, however, that many samples showing rotations from −49° to −53° with the sodium line, when assayed physiologically, show only 64–88 per cent. of the standard. It is therefore necessary to carry out a physiological test, especially when the adrenaline has been prepared synthetically. The standard used is a sample of pure crystalline laevo-rotatory adrenaline issued under the auspices of the Health Organisation of the League of Nations. For the test either the decapitated cat or the anaesthetised atropinised dog may be used. We have employed the former preparation, which is made as described for the test of the pressor hormone of pituitary posterior lobe extract.

The standard preparation should be dissolved in water, brought to an acidity of p_H 2 by means of hydrochloric acid, at a concentration of 0·1 per cent. The further dilution of this and other preparations of similar concentration is usually 1 in 100, and should be made with 0·9 per cent. sodium chloride solution, acidified to p_H 2 with hydrochloric acid. Such a dose of the standard should be selected as will just produce a submaximal rise of blood pressure; 0·0005 mgrm. is commonly the most suitable dose, but this may vary between 0·002 and 0·01 mgrm.

The test differs from that of the pressor hormone of pituitary posterior lobe extract in the fact that doses can be given at intervals of a few minutes. Once the standard dose has been chosen, it should be given throughout alternately with a dose of the sample under examination. It is essential to repeat each dose at least once, and an assay can be considered satisfactory only when doses of the unknown have been found which give rises of blood pressure just less than, equal to, and just greater than, those produced by injections of the dose of standard.

The United States Pharmacopoeia recommends the use of anaesthetised atropinised dogs. The general principles of the assay are exactly the same as when the decapitated cat is used. The sample under examination is compared with a solution of standard epinephrine.

J. C. Munch and W. A. Deckert (*J. Amer. Pharm. Ass.*, 1930, **19**, 354) found that procaine increased the sensitiveness of the dog to a subsequent injection of adrenaline. In carrying out the test, therefore, a series of doses of the solution of standard adrenaline is first given to determine the sensitivity of the animal, and this is followed by a single injection of the solution under test. The pressor response given by the latter is then equated to that given by one of the doses of standard.

THYROXINE AND DRIED THYROID

As we consider the chemical test a more suitable method of assay, we shall not do more than mention that three different methods of physiological assay are available, namely, the acetonitrile test, the tadpole test, and the mouse metabolism test. In the first the potency of the preparation is determined by its power of increasing the resistance of mice to acetonitrile, in the second by its effect in accelerating metamorphosis of tadpoles with corresponding decrease in size, and in the third by its influence in stimulating the output of carbon dioxide and consumption of oxygen. The errors of these methods are about 30 per cent. The Health Committee of the League of Nations have recommended the acetonitrile test, and have proposed the use of a preparation of thyroid gland containing 0·2 per cent. iodine in specific combination as the standard. (E. Knaffl-Lenz, *Publications of the League of Nations*, III, *Health*, 1928, III, 10, Ch. 734, p. 35.)

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Notes on the Use of the Hortvet Apparatus in Determining the Freezing-Point of Milk

BY H. C. LOCKWOOD, B.SC., A.I.C.

(*Read at the Meeting, April* 6, 1932)

THE Hortvet apparatus,* as supplied, lacks various refinements necessary for rapid and accurate determinations. The following modifications are therefore suggested.

ELIMINATION OF PARALLAX.—Accurate readings to a thousandth of a degree are difficult with a solid-stem thermometer, owing to marked parallax. This is aggravated by the attached lens, especially as the lens can be swivelled in all directions. The error was avoided in the following manner:

A horizontal pointer, AB, made of sheet metal, was fixed radially on the frame of the lens at C, the point nearest the thermometer stem. The pointer extended across the face to the centre of the lens, and the other end was of sufficient length just to touch the thermometer when turned to its nearest position by swivelling the bracket, D. The lens must always be used in a vertical plane, parallel with the thermometer, and all adjustment is obtained by swivelling and sliding on the main supporting pillar. Any adjustment which throws the plane of the lens out of the vertical must be avoided. Some of the fitments supplied appear to be superfluous.

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* A general description of the Hortvet apparatus is given by Elsdon and Stubbs (*J. Soc. Chem. Ind.*, 1931, 50, 135–141T, and they append a comprehensive list of references.

A convenient way of arranging the thermometer parallel with the main lens support, E, is as follows:—The pillar, E, is sighted with each of the two parallel edges of the back-board of the instrument and should be found parallel by construction. If not parallel, the pillar should be adjusted.

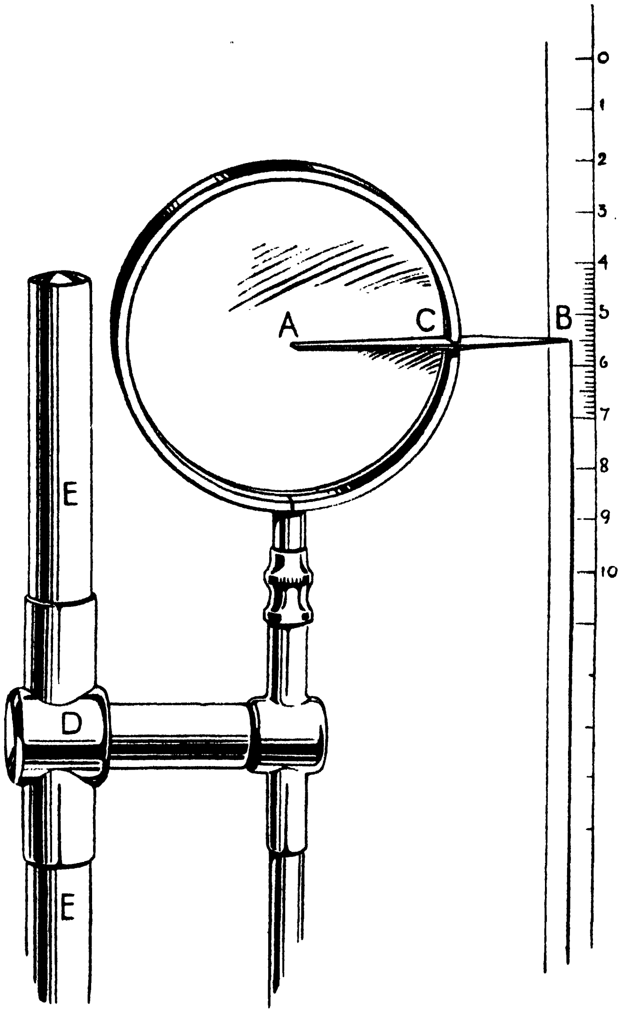

Fig. 1

When the thermometer is inserted, it is necessary to sight it against each edge of the back-board of the instrument, and adjust it until parallel. A certain amount of adjustment is given by the freezing-point tube, but large deviations would have to be overcome by re-fitting the large metal tube in the cork, or by packing the Dewar flask. The correct position, having been once found, is easily re-obtained for subsequent determinations. In Fig. 1 the pointer, AB, being at right angles to the pillar, E, is made, therefore, to move at right angles to the thermometer, and when the lens bracket, D, is swivelled, the pointer, AB, moves in a plane at right angles to the thermometer. Thus, if B, the end of the pointer, touches the thermometer opposite the top of the column of mercury, and the bracket is then swivelled on pillar, E, as described later, the pointer, AB, is in the plane at right angles to the stem of the thermometer containing the top of the column of mercury. If the reading is then taken through the centre of the lens at A, the eye, A, and the top of the column of mercury are in a straight line at right angles to the stem of the thermometer, and parallax is thereby avoided.

In the determination the column of mercury is watched until stationary after the necessary tapping of the thermometer. The lens is then adjusted by turning and sliding the split sleeve, D, on the main support, E, so that the pointer touches the thermometer stem and is level, as near as can be judged, with the column of mercury. The inaccuracy introduced here is of the same order as that due to parallax, which may amount to *plus* or *minus* five-thousandths of a degree. The main pillar, E, is then firmly clasped by the left hand, the thumb-nail being placed under the sleeve so that it acts as a guide when the lens bracket is turned through approximately 90°. The eye is then placed at such a distance from the lens (say 6 inches),that it can focus the thermometer and yet see the pointer at the centre of the lens. The eye is then moved up or down until the centre point corresponds with the top of the thread, when the reading can be made conveniently with complete avoidance of parallax. By this method the reading is taken at right angles to the stem of the thermometer, and different observers agree to a thousandth of a degree.

The increase in the accuracy of the reading can be calculated, as follows, by consideration of Fig. 2, where the dimensions shown are based on the particular apparatus at present in use:

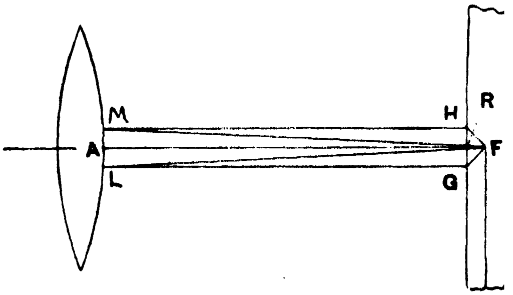

Fig. 2

In Fig. 2 F is the top of the column of mercury, and R is the correct reading to be obtained, the line RF being at right angles to the stem of the thermometer. By actual experiment it was found that the inaccuracy due to parallax may amount to ±0·005°, which, in actual measurement, equals 1 mm. (1° C. = 10 cm.). The pointer, AB, of Fig. 1, can be made to touch the thermometer near the correct reading, R, with this degree of accuracy, and this is shown exaggerated in the diagram as HG, where HG represents 1 mm. or 0·01° C. The lines HM and GL are at right angles to the stem of the thermometer, and represent the movement of the pointer, AB, when the lens-bracket is turned on the main supporting pillar. The points M and L give the maximum variation of A, the centre of the lens, when taking the reading of F. By joining M and L to F, two lines are given which cut the graduations on the stem of the thermometer a little above and below R, the correct reading to be obtained. The accuracy of the reading depends on the amount of scale intercepted by the angle MFL, since the eye is kept within this angle by the pointer at the centre of the lens.

By actual measurement the thermometer stem is 9 mm., so that RF = 4·5 mm., and HG is 1 mm. When the lens-bracket is turned to take the reading, the distance of the centre of the lens to the thermometer thread, AF, is 100 mm. Hence in the triangle MFL, the intercept of $\angle$MFL on G

$$= \text{ML}\,\frac{\text{RF}}{\text{AF}}$$

$$= 1\,\frac{4\cdot 5}{100}\ \text{mm., since ML} = \text{HG} = 1\ \text{mm. on assumption,}$$

$$= 0\cdot 045\ \text{mm., } \textit{i.e. } 0\cdot 00045^\circ\text{, since } 1\ \text{mm.} = 0\cdot 01^\circ\ \text{C.}$$

Hence, on the assumption that the reading can be taken unaided to 0·01° C., the accuracy, by the use of the pointer, is increased to 0·45-thousandths, an increase of at least twenty times. The reading is, therefore, easily obtainable to a thousandth of a degree.

In this proof the refractive index of the thermometer-stem has not been taken into account, as all the rays are practically at right angles to the thermometer stem, and thus suffer very little refraction.

STIRRING.—The rate of stirring should be fairly uniform during supercooling, and a speed of approximately one complete stroke a second was found suitable. Under these conditions the liquid under examination was kept in a fair degree of motion, and it was very exceptional for the freezing to start of its own accord before the liquid had been sufficiently supercooled, as often happens with erratic stirring. With the stirrer supplied this was found very tiring, as the arm had to be held out unsupported about 18 inches above bench level while the stirring was maintained for five or ten minutes during a determination.

A small pulley was attached to the thermometer-stem a short distance above the zero, and a light string was fastened to the stirrer, and passed over the pulley and down through a guide to the bench. A loop was made in the end of the string, so that when the loop touched the bench at a convenient place by pulling, the stirrer was at the top of its stroke, which could be pre-determined by noting the position of the handle with regard to the graduations of the thermometer. By inserting a finger in the loop it was necessary only to raise the finger three inches above the bench and then lower it, to obtain a complete stroke of the stirrer. This operation can be regularly maintained without fatigue. A small coil-spring was fitted on the stirrer between the handle and the guide to prevent the stirrer from bumping on the bottom of the tube. This way of stirring is much less tiring, but still has the disadvantage that during the tapping of the thermometer and the seeding, the stirring has to be discontinued for a short time, as both hands are engaged.

VOLUMES OF LIQUID NECESSARY FOR THE TEST.—To obtain identical conditions it is necessary to use the same volume of liquid for each test, and, to save measuring the liquid in a cylinder, whereby the cooled liquid would be warmed considerably, a mark has been made on the boiling-tube to indicate the volume necessary so that when the thermometer is inserted, the bulb will be submerged to the lower mark.

It is also difficult to judge the amount of alcohol in the metal tube, but a suitable depth having been found, a graduation can be made on the ether gauge-tube, which is then used as a dipstick.

THE USE OF PRESERVATIVES.—It is frequently most desirable that milk samples should be submitted from the laboratories in the milk-producing areas to the main laboratory for confirmation.

The potassium chromate preserving pellets, often used, were tried with regard to their suitability for the freezing-point test. It was found that one tablet, weighing 0·117 grm., when dissolved in half-a-pint of water or milk, lowered the freezing-point, on an average, by 0·008° C., and also increased the acidity by 0·4 c.c. *N*/10 sodium hydroxide solution for 20 c.c. Even when three chromate tablets were used with half-a-pint of milk the acidity began to increase after the second day of storage at room temperature. The addition of three tablets to the half-pint of milk would lower the freezing-point by 0·024° C., representing 4 or 5 per cent. of water, and the analytical figures would also be influenced, giving an enhanced figure of 0·4 on the density, resulting in an increase of 0·1 per cent. in total solids, though the fat would remain unaltered. Too many corrections are necessary for this preservative to be adopted in determining the freezing-point of milk.

It was considered desirable to obtain a preservative having a freezing-point of —0·55° C., so that its addition to pure milk would probably not affect the freezing-point. After several preliminary experiments, a solution of formaldehyde was found which satisfied various requirements and had the great advantage of being practically neutral to phenolphthalein.

The preparation of the formaldehyde solution was found not to be as required by theory from the simple formula H.CHO, since the 40 per cent. solution contains, besides the volatile H.CHO, such compounds as the hydrate $CH_2(OH)_2$, and polyhydrates such as $(CH_2)_2O(OH)_2$. On dilution of the formalin, decomposition and molecular re-arrangement take place, and is complete in twenty-four hours, as shown, when 2 c.c. of 40 per cent. formaldehyde to 100 c.c. are used.

Time	Δ °C.
½ hour	0·385
1½ hours	0·550
24 hours	0·630
4 days	0·624

The 2 per cent. solution was further diluted by the calculated amount to give a freezing-point of — 0·55° C. This solution was found to have good keeping properties as shown below.

Time	Δ °C.
After diluting first solution	0·553
1 month	0·555
3 months	0·555

Occasionally a little difficulty is experienced in obtaining good duplicate readings on formaldehyde solutions, and variations may amount to 0·01° C., but, by allowing plenty of time for thawing, or by changing the solution in the boiling-tube, this difficulty is overcome. Such divergence is not of any practical importance, since only 1 c.c. of the solution is added to 100 c.c. of milk.

In preparing the stock solution, 18 c.c. of 40 per cent. formaldehyde are diluted to 1 litre and, after standing for twenty-four hours, the freezing-point is taken and the necessary dilution made. The addition of this solution to pure milk has no effect on the freezing-point, no matter in what proportion it is added. Tests were made with various amounts in order to ascertain the preserving properties.

Volume of preservative added to 100 c.c. of milk c.c.	Temperature of room during the test °F.	Age of milk when sour Days
0·5	60–70	3
1	60–70	4
2	60–70	6
2	75	3

Methyl red is a useful indicator to determine whether a sample of milk is too sour for the freezing-point test. So long as a red colour is not given on adding 0·1 c.c. of a 0·1 per cent. of that indicator to a small amount of milk in a test-tube, the sample can be considered suitable.

Several investigators have attempted, by titrating with $N/10$ sodium hydroxide solution, to apply a correction for the acidity of milk, but their results differed widely, varying from 0·0013° to 0·0021° C. for every 0·1 c.c. of $N/10$ sodium hydroxide solution used for 20 c.c. milk, after subtraction of the amount normally required by the milk (3 or 4 c.c.). Such a variation in the factor makes the correction unreliable, and it is better to preserve the sample.

The effect on the analysis of adding formaldehyde solution was considered, and milk to which 2 c.c. of the solution per 100 c.c. had been added, gave results which, after correction for dilution, agreed with the original sample within experimental error. The specific gravity of the formaldehyde solution was 1·002.

The addition of 1 c.c. of formaldehyde solution to 100 c.c. of milk will make no detectable difference in the determination of fat, and the density can be corrected by adding 1 per cent. of the significant figures; *e.g.* 1032·1 gives 1032·1+0·3=1032·4. This addition of formaldehyde will make practically no difference to the freezing-point of watered milk, since with 20 per cent. of added water it will lower it by only 0·001° C., and for 40 per cent. of added water by 0·002° C.—figures well within the accuracy required. It is considered very unlikely that such gross adulteration as the latter will occur.

In conclusion, I am indebted to Messrs. Cadbury Bros., Ltd., for permission to publish this portion of the research on the freezing-point of milk, which was carried out in their laboratories at Bournville.

The Separation of Aluminium as Phosphate in the Presence of Calcium Phosphate, with Special Reference to the Action of Milk on Aluminium

By A. G. C. GWYER, Ph.D., and N. D. PULLEN, A.I.C.

There seems to be a great difference of opinion as to the best method of determining aluminium when it occurs as a phosphate in the presence of calcium phosphate. In such case the method of Carnot, or some modification of it, seems to be in general use. As is well known, this method consists in the precipitation of aluminium as the neutral phosphate from a solution rendered slightly acid with acetic acid. In the absence of calcium no particular difficulty arises, but it does not seem to be generally recognised that, in the presence of calcium, the degree of acidity at which the aluminium is precipitated is very important and even crucial.

Aluminium phosphate itself begins to precipitate at a p_H value of about 3·5, whereas calcium phosphate precipitates at p_H 5·7–6·0. It would appear, therefore, that, so long as the solution is rendered slightly more acid than 5·7, aluminium phosphate should precipitate free from calcium. We have found, however, that this is not the case, and it will be shown that, unless the acidity is increased to p_H 4·5 or 4·0, calcium contamination will occur, and the results obtained for aluminium will be rendered worthless.

In the work which we had in hand it was desired to determine small amounts of aluminium in the presence of relatively large amounts of calcium, and the experiments here described were designed with that end in view.

The determination may be carried out in one of two ways. (*a*) Removal of the calcium first and determination of the aluminium left in the filtrate; (*b*) direct precipitation of the aluminium under conditions which ensure that the whole of the calcium remains in solution.

The first method is not entirely satisfactory with only small quantities of aluminium in the presence of relatively large quantities of calcium, as it is rather difficult to examine the calcium precipitate for traces of aluminium carried down with it. But with the second method it is a perfectly simple matter to examine the aluminium precipitate for traces of calcium. For this reason we have confined our attention to the second type of separation.

Experimental.—For the first part of the experiments on methods of separation, synthetic solutions were prepared containing—(A) 0·00139 per cent. of aluminium (as sulphate), and 0·375 per cent. calcium (as phosphate); (B) 0·00139 per cent. of aluminium (as sulphate) only.

Method I: Precipitation of Aluminium by Hydroxyquinoline.—To 100 c.c. of each of the above solutions 10 c.c. of 40 per cent. sodium acetate solution were added, and the liquid was neutralised with ammonia, and then acidified with acetic acid. Three c.c. of 2 per cent. hydroxyquinoline acetate solution in 5 per cent. acetic acid were then added, drop by drop, and the mixture was maintained at 70° C. for 2 hours, and then allowed to stand for a further 2 hours. The precipitates were filtered off on Jena glass filters and dried at 110° C. before weighing.

Taken	*Taken*
A. 0·00139 per cent. of aluminium	B. 0·00139 per cent. of aluminium
0·375 ,, ,, ,, calcium	
Found	*Found*
A. 0·0004 per cent. of aluminium	B. 0·00137 per cent. of aluminium
0·0004 ,, ,, ,, ,,	0·00126 ,, ,, ,, ,,

In the solutions A, both calcium and aluminium phosphates are precipitated on neutralisation and remain, in colloidal state, on addition of acetic acid. As a result, practically no hydroxyquinoline compound is formed.

This determination was then repeated with weaker solutions—

Taken	*Taken*
A. 0·0005 per cent. of aluminium	B. 0·0005 per cent. of aluminium
0·1 ,, ,, ,, calcium	
Found	*Found*
A. 0·0003 per cent. of aluminium	B. 0·0006 per cent. of aluminium
0·0002 ,, ,, ,, ,,	0·0005 ,, ,, ,, ,,

The above results show that, whilst the hydroxyquinoline method is quite satisfactory for solutions of aluminium only, it is useless where calcium is present in relatively large amounts.

METHOD II: CARNOT'S METHOD.—One hundred c.c. of the test solution (*infra*) were neutralised with ammonia to methyl orange, and sulphur dioxide was passed in until the precipitate redissolved (Fe$^{\cdot\cdot\cdot}$ also reduced to Fe$^{\cdot\cdot}$). Sodium phosphate (0·2 grm.) and sodium acetate (5 grms.) were then added, and the solution was boiled until free from sulphur dioxide. The precipitate was then filtered off, washed, re-dissolved in hydrochloric acid, and re-precipitated as above, but without the addition of the sodium phosphate. After being washed, dried and ignited, the precipitate was weighed as aluminium phosphate.

Taken

0·00139 per cent. of aluminium (as sulphate)
0·375 ,, ,, ,, calcium (as phosphate)

Found

1. 0·00312 per cent. (as aluminium)
2. 0·0016 ,, ,, ,, ,,
3. 0·00184 per cent. (as aluminium)
4. 0·00124 ,, ,, ,, ,,

Further examination of these precipitates showed calcium contamination in each case.

METHOD III.—A series of tests was then made with modifications of Method II, the p_H of the solution being carefully adjusted to 4·5 by means of acetic acid and sodium acetate.

As the results show, the amount of acetic acid to be added is critical, depending upon the amount of calcium present, and, unless sufficient acid is present, erroneous results will be obtained.

For preliminary tests the following solution was prepared:—0·00137 per cent. of aluminium (as sulphate); 0·05 per cent. of calcium as phosphate (approx.).

The aluminium was precipitated by adding 1 c.c. of acetic acid and 1 c.c. of saturated sodium phosphate solution, and dropping 40 per cent. sodium acetate solution into the hot mixture until the precipitate formed began to flocculate. The solution was then heated for a while, and the precipitate was separated, dried, ignited, and weighed as aluminium phosphate.

With this solution it was found that, provided the amount of acetic acid added was not less than 1 c.c., practically theoretical results were obtained.

A second solution was then prepared containing the same amount of aluminium, but twice the amount of calcium. The results from this were interesting, in that they showed that, unless the amount of acetic acid added was increased to 5 c.c., a large white precipitate of calcium phosphate came down, although the p_H of the filtrate still remained below 5·0.

As this appeared to be the solution of the problem, the experiments were repeated under more carefully controlled conditions.

Taken.—0·00137 per cent. of aluminium as sulphate; 0·1 per cent. of calcium as phosphate.

Found.—(*a*) With 1 c.c. of acetic acid, 1 c.c. of sodium phosphate solution, 10 c.c. of sodium acetate solution.

Weight of ppt. (1) 0·3414 grm. containing 0·0764 grm. calcium, 22·4 per cent.
(2) 0·3123 ,, ,, 0·0704 ,, ,, 22·5 ,, ,,
Filtrate (1) 0·0168 grm. of calcium (p_H 4·9).
(2) 0·0226 ,, ,, ,, (p_H 4·85).

(*b*) The experiments were then repeated, this time with the use of 5 c.c. of acetic acid, instead of 1 c.c., with the following results:

Weight of ppt. as aluminium phosphate—
(1) 0·0067 grm. = 0·00132 per cent. of aluminium.
(2) 0·0069 ,, = 0·00134 ,, ,, ,, ,,

Calcium in filtrate—
(1) 0·0964 per cent. of calcium (p_H 4·5).
(2) 0·0956 ,, ,, ,, ,, (p_H 4·5).

Actual calcium content of original solution 0·0964 per cent.

These results show definitely that complete separation of aluminium and calcium phosphates can be effected, provided that the correct amount of acetic acid is added to give a p_H between 4·0 and 4·5; with higher values for p_H calcium phosphate begins to come down, giving unreliable results.

We wish to draw particular attention to these results for the following reasons: The solution, as made up, contains practically the same amount of calcium as is found in fresh milk, *viz.* 0·1 per cent. The determination, made as under (*a*), gave a white precipitate weighing some 0·34 grm., and, considering that the precipitation was made in a solution of a p_H value* below 5·0, there would appear to be a certain amount of justification for assuming such a precipitate to consist of aluminium phosphate where the actual amount of aluminium present was unknown. Actually the precipitate is shown to consist of calcium phosphate, but, on the assumption that it is aluminium, then, by calculation, an aluminium content of 120 grains per gallon in the original solution is obtained.

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* The p_H was determined colorimetrically, bromphenol blue being used as indicator. The standard was prepared from a similar solution checked against a hydrogen electrode.

ACTION OF MILK ON ALUMINIUM.—Tests on the action of milk on aluminium have been carried out from time to time by various investigators. In most cases no action is reported, but, from time to time, there have appeared rather alarmingly high results, which appear to show that milk has a marked solvent action on the metal. It would now appear, however, that these results could be readily explained by the effect of the calcium, as shown above. It is true that in some text-books it is stated that, provided the p_H of the solution is kept below 6·0, precipitation of calcium does not take place. But we have shown above that this is incorrect, which makes it appear extremely likely that, had these precipitates been further examined, they would have been found to consist very largely of calcium phosphate and not of aluminium phosphate alone.

Experiments were then carried out by the modified methods of separation given above, to find how much aluminium, if any, is taken up by milk during the normal process of boiling in an aluminium pan.

The tests were made with fresh milk, new pans taken from stock, and an old pan which had been in continual use for more than 12 months.

The experiments were as follows:—A measured quantity of fresh milk (250 c.c.) was heated in the pans to boiling-point, allowed to boil for about two minutes, and then poured into an evaporating dish, evaporated to dryness, and very carefully ashed. The ash from each sample was dissolved in hydrochloric acid, and the solution was neutralised with ammonia and treated with acetic acid, acetate, etc., and the precipitate was weighed as aluminium phosphate.

The following results were obtained when 5 c.c. of acetic acid were used:

	Weight of final ppt. Grm.
Blank on fresh unboiled milk ..	0·0002
Milk boiled in new pans ..	0·0002
,, ,, ,, old ,, ..	0·0002

These figures show that milk, when boiled in aluminium vessels, exerts no action whatever on the metal.

SUMMARY.—Experiments on the gravimetric estimation of aluminium as phosphate in the presence of calcium phosphate show that entirely erroneous results are obtained unless the acidity of the solution in which the precipitation takes place is very carefully adjusted. The p_H should not be less than p_H 4·5, obtained by the use of acetic acid and sodium acetate. It should be noted, however, that with increasing amounts of calcium in the presence of relatively small amounts of aluminium large amounts of acetic acid are required.

Other experiments, on the action of milk boiled in aluminium vessels, have shown that no action whatever takes place. (The modified method given in the text was used for the determination of any aluminium present.)

We wish to thank the British Aluminium Co., Ltd., for permission to publish these results and also Miss M. Bulling for help in carrying out a large number of determinations.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE DETECTION OF ADULTERATION OF INDIAN COFFEE, WITH SPECIAL REFERENCE TO THE EXTRACT METHOD

In the course of investigations carried out on standards for coffee for official adoption under the Burma Food and Drugs Act, the average aqueous extract obtained with Indian coffee was found to be 28·0 per cent., which is somewhat higher than the generally accepted figure of 24·0 per cent. for genuine samples. This led to the assumption that the degree of roasting might appreciably influence the figure.

Accordingly, a graduated series of six samples was prepared from the authentic raw beans, the period of roasting being varied from 15 minutes to an hour-and-a-half, respectively. The samples were ground, and the extract was determined on 5 grms. of the dried sample in the usual way.

The percentage extract thus obtained showed a gradual decrease with increase in the time of roasting, the maximum being 28·8 per cent., and the minimum 27·9 per cent. It cannot be said, therefore, that the degree of roasting influences the result to any marked extent, if carried out within practical limits. It certainly does not account for the discrepancy noted above.

A modification of the usual formula for the estimation of chicory in coffee has, therefore, been found necessary in this laboratory. The average percentage extract of 70 for roasted chicory was substantially confirmed. Under these conditions the percentage of chicory present in a given sample is expressed by the equation: $x = \frac{E - 28}{0{\cdot}42}$, where x represents the percentage of chicory, and E the percentage of extract found. (*Cf.* E. W. T. Jones in Johnson's "*Analyst's Laboratory Companion*," 1920, p. 157, who, however, used a less complete extract.)

Although chicory is often employed to adulterate coffee in Burma, ground roasted gram (*i.e. Cicer arietinum* L., the common gram or chick pea) is more widely used. Sometimes both these substances are present in varying proportions. Chicory is darker than coffee, whereas gram possesses a rather paler tint. The reason for these mixtures, therefore, will be obvious.

Roasted gram is most readily detected by a microscopical examination of the sample. The palisade cells are of somewhat variable length, and, still remaining more or less attached to each other, are characteristic. The parenchyma and starch grains are similar to those of the common pea, though some of the starch grains are distorted, and present the usual features to be observed after subjection to excessive heating.

The extract method is of no use for the quantitative estimation of gram when used as an adulterant, as the extract figure is too near that obtained for coffee. After being detected by the microscope the adulterant may be estimated by determining the starch present, of which it contains 50 per cent.

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THE ANTIMONY TRICHLORIDE TEST FOR VITAMIN *A*

WHEN oils are tested for vitamin *A* with Carr and Price's antimony trichloride reagent, the possibility of the presence of dissolved colouring matter which may react with this reagent should not be overlooked.

Certain oil-soluble aniline dyes give intense carmine to violet colorations with antimony chloride. Thus, when "medicinal" paraffin, coloured with an oil-soluble yellow dye to give a tint about equal to that of an average cod-liver oil, was tested with the antimony trichloride reagent in the usual way, a carmine coloration was obtained. "Medicinal paraffin" itself is quite inactive towards this reagent.

It is true that the colours obtained were not the blue which is given by cod-liver oil, but, as only four aniline dyes were tried, it is possible that other oil-soluble yellow, orange or brown dyes may give blue colorations with the reagent. The coloration nearest to the cod-liver oil blue was obtained with turmeric, which gave a bluish-violet colour. The colorations obtained with aniline dyes are stable towards heat and light, but that given by turmeric is unstable.

The dyes tested behaved in the same way towards brominated phenols, which react with oils and fats giving colours with the antimony trichloride reagent, as I have already described (ANALYST, 1931, **56**, 104).

A. F. MCCARLEY

BIRLING, HARTON LANE,
SOUTH SHIELDS

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* The Publication Committee wish to draw special attention to this Bibliography, which has been compiled by Mr. T. H. Pope at their request. Section II, on Lead, will appear in the December issue.—EDITOR.

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Drabkin and Waggoner. Maintenance and Production of Haemoglobin on Synthetic Diets: Determination of Copper. *J. Biol. Chem.*, 1930, **89**, 51; *B.C.A.*, 1931, 247a. [Precautions in using Biazzo's method (*Annali Chim. Appl.*, 1926, **16**, 96) and the potassium ethyl xanthate method.]

Dutoit and Zbinden. Spectrographic Analysis of the Ash of Blood and of Organs. *Compt. rend.*, 1929, **188**, 1628; *B.C.A.*, 1929, 952a.

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Elvehjem and Hart. Drabkin-Waggoner Modification of the Biazzo Method for Determining Copper. *J. Biol. Chem.*, 1931, **91**, 37; *C.A.*, 1931, 3697.

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Elvehjem and Lindow. Determination of Copper in Biological Materials. *J. Biol. Chem.*, 1929, **81**, 435; Analyst, 1929, **54**, 245. (Colorimetric, with chloroform solution of the precipitate formed with potassium thiocyanate and pyridine.)

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Flinn and Inouye. Some Physiological Aspects of Copper in the Organism. *J. Biol. Chem.*, 1929, **84**, 101; Analyst, 1929, **54**, 758. (Copper in small amount beneficial to guinea-pigs.)

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Fox and Ramage. Spectrographic Analysis of Animal Tissues. *Nature*, 1930, **126**, 682; *B.C.A.*, 1930, 1609a. (Copper of common occurrence.)

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Gebhardt and Sommer. Determination of Copper in Dairy Products. *Ind. Eng. Chem., Anal. Edit.*, 1931, **3**, 24; *B.C.A.*, 1931, 316b. (Colorimetric.)

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Gorter, Grendel, and Weyers. Part played by Copper in the Anaemia of Children. *Maandschrift Kindergeneeskunde*, 1931, **1**, 70; *C.A.*, 1932, 1335. (Copper-contents of bloods given.)

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Hellwig and Quam. Copper Content of Beef and Hog Tissue. *Food Ind.*, 1930, **2**, 411; *C.A.*, 1931, 4631. (Xanthate method used.)

Hertwig. Determination of Zinc and Copper in Gelatin and Glue. *J.A.O.A.C.*, 1923, **7**, 41; *J.S.C.I.*, 1923, 1034a. (Copper determined volumetrically.)

Hess, Supplee, and Bellis. Copper as a Constituent of Milk. *J. Biol. Chem.*, 1923, **57**, 725; Analyst, 1924, **49**, 41. (Colorimetric, with potassium ethyl xanthate.)

Hirano and Mikumo. Copper in the Legumes. *J. Pharm. Soc. Japan*, 1925, No. 525, 992; *C.A.*, 1926, 616. (Colorimetric with ammonia.)

Hochstadter. Determination of Ash, Arsenic, Copper and Zinc in Gelatin. *Ind. Eng. Chem.*, 1923, **15**, 1197; *C.A.*, 1924, 30.

Hugues. Copper Contents of Wines. *Prog. Agr. Vit.*, 1931, **95**, 472; *C.A.*, 1931, 4344.

Inouye and Flinn. Determination of Copper in Biological Material. *J. Lab. Clin. Med.*, 1930, **16**, 49; *B.C.A.*, 1931, 990a. (Electrolytic.)

Järvinen. Colorimetric Estimation of Small Quantities of Metals in Foodstuffs and the Preliminary Destruction of the Organic Matter. *Z. Nahr. Genussm.*, 1923, **45**, 183; *J.C.S., Abs.*, 1923, ii, 655. (Method for copper given.)

Janicsek. Copper-content of Drugs arising from Spraying. *Magyar gyógysz. Tdras. Ertes.*, 1929, **5**, 317; *B.C.A.*, 1930, 348b. (Electrolytic.)

Keilholz. Determination of Some Metals and of Arsenic in Plant and Human Organs. *Pharm. Weekblad*, 1921, **58**, 1482; *J.C.S., Abs.*, 1921, ii, 708. (Scheme of analysis for arsenic, copper, manganese, zinc, aluminium, and lithium given.)

King. The Industrial Contamination of Food with Copper. *Ind. Eng. Chem.*, 1927, **19**, 1004; Analyst, 1927, **52**, 723. (Nickel interferes with colorimetric xanthate determination.)

King and Etzel. Copper as an Industrial Contamination in Foodstuffs. *Ind. Eng. Chem.*, 1927, **19**, 1004; *B.C.A.*, 1927, 973b.

Kleinmann and Klinke. Copper Content of Human Organs. *Arch. path. Anat. Physiol.*, 1930, **275**, 422; *B.C.A.*, 1931, 1321a. (Ethyl bromide used instead of chloroform in Schönheimer and Oshima's method.)

Krebs. Copper in Human Blood-Serum. *Klin. Wochenschr.*, 1928, **7**, 584; *B.C.A.*, 1928, 1391a.

Lampitt, Hughes, Bilham, and Fuller. Determination of Copper in Foodstuffs. Analyst, 1926, **51**, 327. (Colorimetric, and gravimetric with quinosol.)

Lasausse. Determination of Copper in Preserved Vegetables. *J. Pharm. Chim.*, 1923, **27**, 290; *J.S.C.I.*, 1923, 469a. (Electrolytic and iodimetric methods.)

Lendrich and Mayer. Occurrence of Arsenic, Lead, and Copper in Fruit and Fruit Products as a Result of Spraying. *Z. Unters. Lebensm.*, 1927, **54**, 137; *B.C.A.*, 1927, 954b.

Liesegang. Detection of Small Amounts of Iron and Copper in Linen, Paper, or Animal Tissues. *Z. wiss. Mikroskop.*, **40**, 14; *C.A.*, 1924, 3572.

Lindow, Elvehjem, and Peterson. Copper Content of Plant and Animal Foods. *J. Biol. Chem.*, 1929, **82**, 465; Analyst, 1929, **54**, 420. (Copper found in 160 human foods.)

Lipman. Chemical Elements indispensable to Plants. *Sci. Monthly*, 1928, **16**, 289; *C.A.*, 1928, 2965. (Copper in small amounts probably essential.)

Lochte and Danziger. Detection of Poisons in the Ashes of Burned Corpses. *Deut. Z. ges. ger. Med.*, 1922, I, 727; *C.A.*, 1924, 207. (Detection of copper considered.)

Lynch, McDonnell, Haywood, Quaintance, and Waite. Poisonous Metals on Sprayed Fruits and Vegetables. *U.S. Dep. Agric.*, 1922, *Bull.* 1027, 1; *C.A.*, 1922, 2006. (Copper [and lead] found in only small amounts, if spraying properly executed.)

McHargue. Copper, Manganese, Zinc, Nickel, and Cobalt as Vital Factors in Soils, Plants, and Animals. *J. Agric. Res.*, 1925, **30**, 193; Analyst, 1925, **50**, 409.

McHargue. Significance of the Occurrence of Copper, Manganese, and Zinc in Forage Crops and Foods. *J. Amer. Soc. Agron.*, 1925, **17**, 368; *C.A.*, 1925, 3330.

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McHargue. Report on (Determination of) Less Common Metals in Plants. *J.A.O.A.C.*, 1930, **13**, 225; *C.A.*, 1930, 3964. (Method for copper.)

Mayrhofer. Rôle of Certain Elements occurring in the Organism. *Pharm. Presse*, 1924, **29**, 69, 78, 106, 114, 122; *C.A.*, 1924, 3629. (Copper determined microchemically with mercurio-ammonium thiocyanate.)

Mehurin. Determination of Ash, Arsenic, Copper, and Zinc in Gelatin. *Ind. Eng. Chem.*, 1923, **15**, 942; *J.C.S., Abs.*, 1923, ii, 891. (Copper: Colorimetric with potassium ferrocyanide.)

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Ministry of Health. Report on the Composition of Commoner British Wines and Cordials, No. 24. Analyst, 1924, **49**, 387. (Copper found in both alcoholic and non-alcoholic wines.)

Miscall, Cavanaugh, and Carodemos. Copper in Dairy Products and its Solution under Various Conditions. *J. Dairy Sci.*, 1929, **12**, 379; *C.A.*, 1929, 5512.

Morrison and Nash. Copper Content of Infant Livers. *J. Biol. Chem.*, 1930, **88**, 479; *B.C.A.*, 1930, 1465A.

Morvillez and Defossez. Reduction of Molybdic Reagents by Cherry Laurel Water. *J. Pharm. Chim.*, 1932, **124**, 27; Analyst, 1932, 581. (Copper constantly present.)

Muttkowski. Copper: Its Occurrence and Rôle in Insects and Other Animals. *Trans. Amer. Micr. Soc.*, 1921, **40**, 144; *C.A.*, 1923, 2154.

Nitzescu. Content of Copper in the Organs of the Human Foetus. *Compt. rend. Soc. biol.*, 1931, **106**, 1176; *C.A.*, 1932, 3016.

Philippi and Hernler. Micro-electrolytic Determination of Copper in Organic Substances. *Microchem., Emich Festschr.*, 1930, 241; *B.C.A.*, 1930, 1546A.

Poirot. Detection of Copper in Distilled Water. *J. Pharm. Chim.*, 1924, [vii], **30**, 393; *J.C.S., Abs.*, 1925, ii, 242. (Colorimetric with guaiacum resin, pyridine, alcohol and hydrogen peroxide.)

Pyriki. Colorimetric Determination of Lead and Copper in Water. *Z. anal. Chem.*, 1924, **64**, 325; Analyst, 1924, **49**, 491. (With slight adjustment, Winkler's ferrocyanide and sulphide method for determining lead and copper simultaneously is satisfactory.)

Quam. Copper Contents of Livers and Liver Extracts. *Proc. Iowa Acad. Sci.*, 1929, **36**, 267; *C.A.*, 1931, 1269.

Quam and Hellwig. Copper Content of Milk. *J. Biol. Chem.*, 1928, **78**, 681; Analyst, 1928, **53**, 542.

Quartaroli. Determination of Minimal Amounts of Manganese, Copper and Iron in Biological Investigations. *Annali Chim. Appl.*, 1927, **17**, 361; *B.C.A.*, 1928, 96A. (For copper, the catalytic effect of the metal on hydrogen peroxide is used.)

Quartaroli. Copper as a Normal Component of Plants. *Annali Chim. Appl.*, 1928, **18**, 47; *B.C.A.*, 1928, 561A.

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Quartaroli. Copper as an Element necessary to Plants. *Annali Chim. Appl.*, 1929, **19**, 467; *B.C.A.*, 1930, 385A.

Ramage. Mushrooms—Mineral Content. *Nature*, 1930, **126**, 279; *B.C.A.*, 1930, 1325. (Copper found in all parts.)

Remington and Shiver. Iron, Copper and Manganese Content of some Common Vegetable Foods. *J.A.O.A.C.*, 1930, **13**, 129; *B.C.A.*, 1930, 392B.

Remy. Normal Occurrence of Copper and Zinc in Foods. *Z. Volksernähr. Diatkost*, 1931, **6**, 21; *C.A.*, 1932, 4105. (Amounts of copper normally present sufficient to maintain ionic equilibrium.)

Ribéreau-Gayon. Iron and Copper in White Wines. *Ann. Falsif.*, 1930, **23**, 535; *B.C.A.*, 1931, 563B.

Rice and Miscall. Copper in Dairy Products and its Solution in Milk under Various Conditions. *Int. Rev. Sci. Pract. Agric.*, 1923, **1**, 1095; Analyst, 1924, **49**, 145. (Colorimetric, with potassium ethyl xanthate.)

Richardson. Determination of Minute Amounts of Lead and Copper in Food, Beverages, etc. Analyst, 1930, **55**, 323. (Colorimetric, with hydrogen sulphide.)

Rosenthaler. Economical Drug Testing. *Pharm. Ztg.*, 1929, **74**, 1279; *C.A.*, 1930, 462. (Microchemical test for copper.)

Roussel and Dufour-Deflandre. Copper Reserves in the Foetal Liver of Vertebrates. *Compt. rend. Soc. biol.*, 1931, **106**, 260; *C.A.*, 1931, 3715. (Detection with diphenylcarbazide.)

Sale. Report on Water. *J.A.O.A.C.*, 1922, **5**, 379; *C.A.*, 1922, 2563. (Copper determined colorimetrically with ferrocyanide.)

Sale. Report on Water. *J.A.O.A.C.*, 1923, **6**, 307; *C.A.*, 1923, 1853. (Methods for zinc, lead and copper, the last colorimetric with ferrocyanide.)

Schindel. Copper Content of Blood. *Klin. Wochenschr.*, 1931, **10**, 743; *B.C.A.*, 1932, 183a.

Schönheimer and Oshima. Copper Content of Normal and Pathological Organs. I. Method; II. Copper Content of Normal and Haemachromatose Liver, Gallstones, and Whole Blood. *Z. physiol. Chem.*, 1929, **180**, 249; *B.C.A.*, 1929, 341a. (Colorimetric, with ammonium thiocyanate and pyridine.)

Schoorl. Examination of Tap Water for Small Quantities of Copper and Lead. *Chem. Weekblad*, 1932, **29**, 338; *C.A.*, 1932, 4661. (Colorimetric determination of copper as sulphide and as ferrocyanide.)

Schuette and Remy. Degree of Pigmentation and its Probable Relationship to the Mineral Constituents of Honey. *J. Amer. Chem. Soc.*, 1932, **54**, 2909; Analyst, 1932, 578. (Copper found in all honeys examined.)

Schütz. Detection of Lead and Copper Salts in Citric and Tartaric Acids. *Pharm. Ztg.*, 1929, **74**, 1127; *B.C.A.*, 1930, 36b. (Critical study of officinal [D.A.B. VI.] German methods.)

Severy. Occurrence of Copper and Zinc in Certain Marine Animals. *J. Biol. Chem.*, 1923, **55**, 79; *J.C.S., Abs.*, 1923, i, 415. (Copper found in 16 marine animals, but not in mammals or clams.)

Sheldon and Ramage. Spectrographic Analysis of Human Tissues. *Biochem. J.*, 1931, **25**, 1608; *B.C.A.*, 1931, 1442a. (Copper universally present.)

Shikata, Tachi, and Hozaki. Application of the Polarograph to the Analysis of Abnormal Mineral Constituents. *Bull. Agr. Chem. Soc. Japan*, 1927, **3**, 52; *C.A.*, 1928, 930. (Determination of copper.)

Shoji. Analysis of Liver Ash by means of the Polarograph. *Bull. Inst. Phys. Chem. Research, Tokyo*, 1931, **10**, 162; *C.A.*, 1931, 4293. (Data for copper.)

Simpson. Minor Elements in Living Organisms. *Chem. Eng. Mining Rev.*, 1932, **24**, 323; *C.A.*, 1932, 4612. (Copper and other elements referred to.)

Smith. Report on Gelatin. *J.A.O.A.C.*, 1923, **7**, 135; *C.A.*, 1924, 716. (Method for copper reported on.)

Spencer. Report on (Determination of) Metals in Foods. *J.A.O.A.C.*, 1931, **14**, 434; *C.A.*, 1932, 774. (Methods for copper discussed.)

Springer. Electrolytic Determination of Copper in Preserved Vegetables. *Z. Unters. Lebensm.*, 1929, **58**, 651; *B.C.A.*, 1930, 529b.

Supplee and Bellis. The Copper Content of Cow's Milk. *J. Dairy Sci.*, 1922, **5**, 456; *C.A.*, 1923, 156. (The potassium ethyl xanthate method found best.)

Taverne. Content of Copper and Zinc in Normal and Carcinomatous Tissues. *Nederl. Tijdschr. Geneeskunde*, 1923, **67**, i, 2810; *J.C.S., Abs.*, 1924, i, 123.

Titus and Hughes. Nutritional Value of Copper in Powdered Dried Milk. *J. Dairy Sci.*, 1929, **12**, 90; *C.A.*, 1929, 1939. (The copper from the vacuum pans may help to prevent anaemia, but tends to destroy vitamins.)

Trotman and Sutton. Determination of the Inorganic Impurities in Gelatin. Analyst, 1924, **49**, 271. (Method for copper given.)

Turnwald and Haurowitz. Heavy Metals of the Human Liver and their Spectrographic Detection. *Z. physiol. Chem.*, 1929, **181**, 176; *B.C.A.*, 1929, 591a.

Van Leeuwen. Copper and Manganese Content of some Vegetable Tissues. *Ann. physiol. physico-chim. Biol.*, 1930, **6**, 178; *C.A.*, 1931, 2171.

Von der Heide. Determination of Copper and Zinc in Wine. *Z. anal. Chem.*, 1925, **66**, 24; Analyst, 1925, **50**, 296. (Both metals precipitated as sulphides and weighed as oxides.)

Walker. Report on (Determination of) Copper (in Foods). *J.A.O.A.C.*, 1930, **13**, 426; *C.A.*, 1931, 357. (Iodimetric method given.)

Walker. Report on (Determination of) Copper (in Foods). *J.A.O.A.C.*, 1931, **14**, 450; *C.A.*, 1932, 775. (Method previously given is satisfactory [*J.A.O.A.C.*, 1930, **13**, 426].)

Warburg. Determination of Copper and Iron, and Copper Content of Blood-Serum. *Biochem. Z.*, 1927, **187**, 255; *B.C.A.*, 1927, 985a.

Warburg. Copper in Human Blood-Serum. *Klin. Woch.*, 1927, **6**, 1094; *B.C.A.*, 1928, 317a. (Colorimetric with ferrocyanide, or catalytically by oxidation of cysteine.)

Warburg and Krebs. Loosely-combined Copper and Iron in Blood-Serum. *Biochem. Z.*, 1927, **190**, 143; *B.C.A.*, 1928, 192a.

Webster and Jansma. Copper-Content of Wheats of Oklahoma and other States. *Science*, 1929, **70**, 174; *B.C.A.*, 1930, 120a.

White. Copper in Tumours and Normal Tissues. *Lancet*, 1921, **201**, 701; *J.C.S., Abs.*, 1922, i, 399. (Copper found in all animal and vegetable tissues examined, especially in degenerating tumours.)

Williams. Determination of Copper and Iron in Dairy Products. *J. Dairy Res.*, 1931, **3**, 93; *C.A.*, 1932, 4385. (After wet ashing, the copper is determined colorimetrically by the xanthate or diethyldithiocarbamate method.)

Wright and Papish. Inorganic Constituents of Milk. *Science*, 1929, **69**, 78; *B.C.A.*, 1929, 953A. (Spectrographic method; copper in unusually large amount found in dried milk.)

Zanda. Significance of Copper in the Animal Organism. *Biochim. terap. sperim.*, 1924, **11**, 7; *J.C.S., Abs.*, 1925, i, 719. (Haematoxylin test and phenolphthalein blood reaction for copper.)

Zbinden. The Infinitely Small Quantities of Certain Elements in Milk and their Detection by the Spectrographic Method. *Lait*, 1931, **11**, 114; *C.A.*, 1931, 4032. (Copper found regularly.)

Zondek and Bondmann. Copper in Human and Cow's Milk. *Klin. Wochenschr.*, 1931, **10**, 1528; *C.A.*, 1932, 184.

T. H. P.

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF LEEDS

Annual Report of the City Analyst for 1931

Of the 3043 samples examined during the year, 1975 were of food and drugs, and, of these, 8·6 per cent. were adulterated.

Black Beer.—Two samples were taken at a shop at the request of the Ministry of Health, as a sample taken at the brewery by the Board of Customs and Excise contained arsenic in excess of the recognised amount. These two samples contained 1/25 and 1/80 grain of arsenic per gallon, respectively, but no action was taken, as this preparation is used as a beverage only after considerable dilution.

Starch in Potted Salmon.—Two samples were reported against, and, in the case of one, which contained 20 per cent. of starchy filling material, proceedings were taken, and costs were obtained against the retailer (*cf.* Analyst, 1931, **56**, 658, 742; 1932, **57**, 382).

C. H. Manley

Fourth National Congress of Pure and Applied Chemistry

The Fourth National Congress of Pure and Applied Chemistry, organised by the Italian Chemical Association, was held in Rome from June 6th to 12th. Dr. Maselli, President of the Association, presided, and there were present more than five hundred members and guests, including representatives of the National Government and of the Governor of Rome, the Prefect, and the delegates of several foreign chemical Societies.

The Society of Public Analysts and Other Analytical Chemists, who had been invited to send a delegate, were represented at the meeting by Mr. A. H. Bennett.

After the speeches of welcome and an account, given by Professor Parravano, of the administration of the fund which had been collected for the promotion of chemical research, the President announced the conferment of the Emanuele Paterno medal on Professor Gustav Tammann, of the University of Göttingen, and Professor Parravano gave a brief account of the medallist's work.

The President's address was devoted principally to a review of the recent progress of chemical industry in Italy, and Professor Tammann delivered a lecture on the behaviour of polonium and thorium B and of their relations with other metals.

The remaining days were occupied by lectures, visits to laboratories and chemical works, and social functions.

Department of Scientific and Industrial Research

REPORT OF THE FOOD INVESTIGATION BOARD FOR THE YEAR 1931*

AMONGST the many researches in progress it is possible to mention only a few. Some of the work of the year has already been published, and the Report gives all references.

PART I

SECTION A. MEAT.—Sheep's liver contains an appreciable amount of vitamin *C*, but when held at −19° C. the activity progressively diminishes. The work of Edsall and Muralt on the physical chemistry of muscle affords good evidence that muscle globulin can be isolated in a condition very little different from that in which it occurs in muscle fibre. The physical changes in muscle when frozen seem to be due to changes in equilibrium between the muscle and its aqueous environment, and the constitution of muscle below the freezing point is mapped out. A study of the kinetics of the oxidation of haemoglobin to methaemoglobin has shown the reaction to be monomolecular with respect to the concentration of haemoglobin, and the rate of oxidation to vary with different samples of blood, and with the hydrogen ion and salt concentration. The work on the Action of Light on Fats (Lea) has been published (*Proc. Roy. Soc.*, 1931, **108**, B, 175); also that on Rancidity changes referred to in the 1930 Report (ANALYST, 1931, **56**, 531). The effect of free fatty acids on the flavour of fats in the absence of rancidity was tested by adding to the fats proportions up to 15 per cent. of the appropriate fatty acids recovered after saponification. When tasted hot, none of the mixtures (even with 15 per cent. of fatty acids) could be distinguished from the controls, and in the cold no harsh or unpleasant flavour was apparent. Attempts to place the Schiff test on a quantitative basis have not proved successful, but the bisulphate method of Tomoda is proving more hopeful.

SECTION B. FRUIT AND VEGETABLES.—In the biochemical study of senescence in apples a comparison of chemical changes in Bramley's seedling and Worcester Pearmain apples stored at 1° C. has involved the compilation and tabulation of many data, including analyses of the soils of various plantations, chemical analyses of the apple tissues, average rate of loss of material in populations during storage, loss of sugar and acid, nitrogen-content, etc. The third series of experiments in connection with the study of sucrose hydrolysis and respiration is primarily a study of the influence of temperature upon the course of chemical change. All apples appear to be free from starch when the sucrose value (glucose and fructose being considered in terms of sucrose concentration) is at 3·0. The state and mode of operation of the sucrose/enzyme/acid system in the living cell and in the *post-mortem* frozen condition are being investigated. The rôle of acetaldehyde in the respiration of plants has been further elucidated. Work on potatoes deals with temperature and metabolic balance and the effect of ethylene on metabolism.

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* Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Pp. 293. Price 5s. 0d. net.

The possibilities of employing atmospheric control for bananas in storage has received attention. Since it has become needful to store fruit under conditions allowing the critical and independent control of humidity and of air movement, a suitable apparatus allowing of these controls has been devised, and is described in detail. Acetaldehyde and ammonia have both been found successful for preventing the rotting of stored fruit, if introduced into the storage atmosphere.

The preservation of fruit and vegetables in the frozen state has received considerable further attention. Partial cooking before freezing at −10° or −20° C., is successful for peas, and the method has been applied to potatoes and runner beans and less successfully to asparagus. In the case of fruit, raspberries stored at −10° or −20° C. without previous heating were perfect in colour and flavour, but plums and cherries, if frozen raw, turn brown and develop an unpleasant flavour on thawing, but previous heating in syrup prevents this. Quick freezing offers no advantages. The work at the Imperial College of Science and Technology has shown that difference in manurial treatment of apples has a greater effect on the chemical composition of the fruit than difference in stocks. Two substances belonging to the hemicellulose class have been isolated, which, together with starch pectin and unhydrolysed residue, make up the insoluble material in the apple.

SECTION C. PORK, BACON, AND HAMS.—The transport of unsmoked, mild-cured bacon from Australia and New Zealand has been found to be impracticable under present commercial conditions, since the fat is rancid after less than 2 months, even if the storage temperature has been as low as −10° C. However, carcases of frozen pork can be successfully transported and used for the manufacture of bacon. The iodine value of pork fat was in every case lower for the inner than for the outer fat, appearing to depend on the temperature at which the pork is laid down. Fast-growing pigs tend to have fat with a low iodine value, and slow-growing pigs to have fat with a higher iodine value; feeding the pig with cod-liver oil appears to make the fat more unsaturated.

SECTION D. BIOLOGICAL ENGINEERING.—Work has been concerned with the rate of evaporation of water from biological materials in cold storage, particularly apples, eggs and cheeses.

The work dealing with loss of water by stored infertile eggs has been extended to deal with variations in individual eggs, and the effect of such factors as thickness and porosity of shell, and the different types of package. The effect of waxing on loss of weight in cheeses was to decrease the overall loss of weight by 30 to 40 per cent., but the saving occurred wholly during the earlier part of storage. The difference in freezing point of egg yolk (−0·57° C.) and of egg white (−0·45° C.) is found to decrease only very gradually on storage, the effect being to set up movement of water from white to yolk, with some distension of the yolk, but the weakening of the yolk membrane is probably largely due to ageing, which is more rapid the higher the temperature.

SECTION E. CANNING.—The work on the corrosion of iron and tin separately has been continued, particularly on the effects of the products of corrosion on the further corrosion of the metals. Ferrous salts greatly accelerate the corrosion of tin in presence of air, and ferric salts accelerate corrosion of iron in presence of air (ANALYST, **1931, 56, 315**), and the combined effect of air and ferric iron is much greater than that of either alone, especially at acidities round p_H 4, as found in many fruit syrups. The effect of oxygen on the rate of corrosion of tin plate is that, with small amounts, tin is attacked most readily at low acidity, but with increase of oxygen the rate of de-tinning becomes greatest at high acidity.

PART II (TORRY RESEARCH STATION)

FISH.—The work on storage of brine-frozen fish described in the last Report has been repeated, and the previous results have been confirmed. These emphasise the need of lower storage temperatures in this country (—20° to —25° C.). Fish stored at such temperatures produces excellent smoke cures. The denaturation of the globulin fraction of the proteins of fish muscle is being particularly studied. The chemical survey of fish oils from both fresh water and marine fish has been continued, and tests for vitamin *A* have been made on both liver and body oils. The liver oil of the halibut is 15 to 75 times as potent in this respect as an average cod-liver oil, and a unique pigmentation discovered in the liver of the angler fish may throw light on the relation between the carotenoid pigments and vitamin *A*.

PART III (DITTON LABORATORY)

ENGINEERING.—The experimental hold has been made to act as a calorimeter for making measurements of the various thermal quantities required for a balance sheet from which the rate of generation of heat by fruit under given conditions of storage can be estimated.

PART IV

The chemical and biological work on fruit at the Imperial College of Science and Technology has been continued.

D. G. H.

Government of Madras

REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1931

THE Chemical Examiner (Lt.-Col. Clive Newcomb, F.I.C.) reports an increase in the total number of analyses (6360 as against 5406 in 1931), the increase being in the amount of medico-legal work.

HUMAN POISONING CASES.—Poisons were identified in 150 of the 340 cases investigated. It is interesting to note that opium is now the most commonly found poison (31 cases), whilst arsenic comes second (21 cases), and organic poisons generally are now nearly twice as common as the inorganic, whereas some twenty years ago the reverse was the case. It is probable that the chief cause for this is that, with the increased spread of education, poisoners are learning that, speaking generally, organic poisons give rise to less characteristic symptoms and are less readily detected afterwards.

Oduvan Poisoning.—In four cases of poisoning by oduvan leaves there was no difficulty in obtaining the characteristic reaction with the leaves themselves, as described in the Report for 1930 (ANALYST, 1931, **56**, 665), but it was found that, by the time the leaves had disappeared from a stomach by digestion or *post-mortem* decomposition, the characteristic reactions had also disappeared. In one case in which a son had introduced the leaves into a curry, in an attempt to poison his father, the reactions were given by the curry.

Madar Juice Poisoning.—The four cases of madar juice poisoning were all suicides. In each examination the stomach-contents were boiled with absolute alcohol under a reflux condenser for an hour and then distilled after the addition of 50 per cent. of sulphuric acid. Each distillate had the peculiar fruity odour which is not decisive proof of madar, but which is more or less characteristic of it, and there is little doubt that this was the poison used (*cf.* ANALYST, 1931, **56**, 665).

Formalin Poisoning.—Cases of formalin poisoning are rare, and there does not appear to be a previous record of one in which formalin was used externally with criminal intent. In one such case during the year a young wife of 15 years of age was severely beaten by her husband and father-in-law, and some corrosive liquid was poured over her head. The liquid caused her great pain, and when she was admitted to hospital some hours later her hair was found to be falling out in locks and the skin of her scalp to be peeling off. The doctor at first suspected that sulphuric or hydrochloric acid might have been used, as the patient's husband belonged to the weaver caste, and this caste also does dyeing and uses these acids in its business. The objects sent for examination were some of the fallen hair, several of the patient's garments stained with the liquid, and a bottle found in the husband's house, and supposed to contain the liquid used. The liquid was formaldehyde of about 31 per cent. strength, and we found formaldehyde on the hair and garments.

Mercury in Viscera and Bones.—Mercury was found in the stomach, intestines, liver, and kidneys, and in one humerus of a body which had been exhumed in a stage of advanced decomposition. It is unusual for bones to be sent for examination for poison, and it is interesting that in this case, where one was sent, mercury was found in it. The reason that the doctor gave for sending it was that he suspected, from a bluish discoloration of the stomach and trachea, that copper had been used, but it was clearly a case of mercury poisoning.

FLORENCE'S TEST FOR SEMINAL STAINS.—Florence's test continues to give reliable results with seminal stains. If, however, the stain contains much albumin, as, for instance, when the semen is mixed with blood, the albumin interferes to some extent with the test by reacting in places with so much of the iodine as to leave too little over for the production of Florence's crystals. If but a small amount of albumin is present, some crystals are generally formed, but fewer, other things being equal, than when albumin is absent. When albumin is present in large concentration the thickness of the precipitate that the iodine forms with it tends to prevent the two solutions from mixing and to obscure any Florence's crystals that are formed. The difficulty can be overcome by diluting the aqueous stain extract to give a sufficient bulk, boiling, filtering and evaporating it to dryness on a water-bath. If the residue is now taken up in one or two drops of water, this solution will give Florence's test. The choline—or whatever substance it is which is responsible for the test—is not destroyed by this procedure, but the spermatozoa are disintegrated and must be looked for in a separate portion of the extract.

BULLET HOLE IN COTTON.—In a shooting case a cotton shirt was submitted with a ragged hole through the breast pocket, and of about the size one would expect from a 450-revolver bullet, and round it was a dark grey mark. The defence suggested that the hole in the shirt might have been made by burning with a hot poker. Experimental shots fired from a 450-revolver into a cotton cloth placed on sand-bags produced holes which agreed in size and shape with the disputed hole, and which had grey marks of the same approximate dimensions at the edges. On analysis, the grey stains in each case were found to consist of lead, whilst the ends of the torn cotton fibres round the holes were, for the most part, unstained, in contrast to holes produced by burning. From these results the conclusion was drawn that the hole in the shirt had almost certainly been caused by a soft lead bullet which had struck it obliquely.

ANAESTHETIC ETHER.—The ferrous thiocyanate test described by Middleton and Hymas (ANALYST, 1928, **53**, 201) is admittedly a very rigorous one, and no specimen of ether in the Madras Government Laboratory would pass it. It is questionable whether this test is not an unreasonably high standard for an ether which has had a voyage to India.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Analysis of Mayonnaise and the Variability of its Egg-Constituents. J. L. Perlman. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 466–482.)—The method suggested by L. C. Mitchell (*ibid.*, 1931, **14**, 418) for the determination of lipoids and lipoid-phosphoric acid in eggs may be adapted to the determination of total fat and lipoids in mayonnaise as follows: 5 grms. of the thoroughly mixed material are weighed by difference into a 100-c.c. Kohlrausch sugar flask, which is kept shaken in a machine while 20 c.c. of a mixture of absolute alcohol and chloroform in equal volumes are slowly added. The agitation is continued until the sample is finely divided (5 minutes), 60 to 65 c.c. more of the solvent being then added, and the shaking continued for 50 minutes. The flask is filled to the mark with the solvent and shaken by hand for 5 minutes, the liquid being next filtered rapidly into a 100-c.c. Erlenmeyer flask, stoppered with a plug of cotton-wool, by carefully inverting the flask on to a funnel fitted with a 9 cm. filter paper. Fifty c.c. of the filtrate are evaporated to apparent dryness in a tall 200-c.c. beaker with the aid of an electric fan. The residue of fat is dried for 10 minutes in an oven at 100° C. and dissolved in 10 c.c. of chloroform, the sides of the beaker being rinsed down with chloroform from a wash-bottle and the liquid filtered through a tight plug of extracted cotton-wool into a weighed platinum dish. The remaining fat is transferred from the beaker to the funnel with the help of chloroform and a stirring rod, adhering solid particles being broken up. The funnel and the tip of its stem are washed into the dish, and the filtrate, which should be clear, is evaporated to dryness in a current of air on a steam-bath; the residue is dried at 100° C. until of constant weight (1·5 to 2 hours) and reserved for the determination of lipoid-P_2O_5.

The fat thus found includes practically all of the egg-yolk lipoids. Analysis of a mixture of 7 fresh eggs gives the value 37·5:1 for the ratio of lipoid to lipoid-P_2O_5, so that multiplication of the P_2O_5-content of the fat residue from the mayonnaise by 37·5 gives approximately the lipoid-content, and subtraction of this from the total fat found yields approximately the true vegetable oil-content. This is, however, not correct for samples stored for any appreciable time without refrigeration.

To determine the lipoid-P_2O_5: For each grm. of the fatty residue in the platinum dish, 5 c.c. of alcoholic potash (8 grms. of KOH per 100 c.c. of 95 per cent. alcohol) are added, and the whole is evaporated to dryness on a steam-bath, and the residue charred as thoroughly as possible over asbestos. The charred mass is treated with excess of nitric acid (1+2), filtered into a tall 200-c.c. beaker, and washed several times with water. The residue is returned to the dish, incinerated until white at or below 500° C., again treated with the nitric acid, filtered off, and washed. The combined filtrates are evaporated to 50 to 60 c.c., and made distinctly alkaline to one drop of phenolphthalein with strong ammonia; the liquid is then neutralised with the nitric acid, 3 to 4 c.c. of this being added in excess. Thirty c.c. of molybdate solution are added, and the mixture kept at

60 to 65° C. for an hour, with frequent stirring, and filtered through a weighed Gooch crucible; the precipitate is transferred with 1 per cent. nitric acid, washed twice with this acid and finally with water, and dried for 2 hours at 110° C. prior to being weighed. Weight of precipitate $\times 0{\cdot}03784 = P_2O_5$.

It was found that, in some of the older samples of mayonnaise, the lecithin had undergone hydrolysis to some extent, the presence of choline being shown by the formation of its insoluble crystalline poly-iodide, photomicrographs of which are reproduced. By means of this test, definite signs of decomposition were detected in more than one-half of a number of samples of mayonnaise from retail shops, and choline was also detected, in proportions increasing with the time, in mixed eggs kept at either ordinary or incubator temperature. As mayonnaise is prepared by a cold process not lending itself to the maintenance of aseptic conditions, it may contain micro-organisms, but the high acidity tends to retard bacterial and mould growth. Products of bacterial action may, however, be present in the separate ingredients prior to mixing. From decomposing whole eggs markedly deficient in lipoid-P_2O_5, bacteria of four different strains capable of hydrolysing lecithin have been isolated. One of these organisms, tentatively named *Bacillus lekitosis*, n. sp., is Gram-positive and spore-forming, and ranges in size from 0·5 × 3 to 0·8 × 6 microns. Besides breaking down lecithin, it ferments dextrose, maltose, and salicin—giving acid but no gas—hydrolyses starch, liquefies gelatin, and effects almost complete proteolysis of milk in about 7 days without giving acid or curd. Under aseptic conditions it destroys the lecithin of mixed eggs almost entirely within about 100 hours at 37° C., this effect being due to an extra-cellular enzyme. T. H. P.

Detection of Hydrogen Sulphide and the Evaluation of the Degree of Freshness of Flesh Products. F. Budagjan. (*Z. Unters. Lebensm.*, 1932, **64**, 226–235.)—The sample is disintegrated and 10 to 15 grms. are packed loosely into the wide end of a small tube (similar to an Allihn calcium-chloride tube), the narrow end being partly closed by a notched cork supporting a strip of filter-paper, 2 mm. wide, on which 1 drop of an alkaline solution of lead acetate is placed. Carbon dioxide is then bubbled through a 6 per cent. solution of copper sulphate and passed rapidly through the tube for 30 minutes in the cold, so that any hydrogen sulphide removed from the sample comes in contact with the strip, whilst the flow of gas as a whole is not impeded. The stain varies from yellow-brown to black, according to the amount of hydrogen sulphide removed, and the results obtained after various periods with fresh and salted beef, mutton, horse-flesh, sausage meat and various fish show that the increase in intensity is a measure of the rate of decomposition, no reaction being obtainable with the flesh of cold-blooded animals and mammals when in a sound state. Since the evolution of hydrogen sulphide does not necessarily accompany decomposition, a negative result should be confirmed by other methods, although a positive result is indubitable. J. G.

Proportion of Tartaric Acid to Free Acid in Natural Moselle, Saar and Ruhr Wine-Musts for the Years 1930 and 1931. F. Seiler. (*Z. Unters. Lebensm.*, 1932, **64**, 278–282.)—Tables show the alcohol-content, total free acidity and tartaric acid for 80 of the musts of these wines at various periods after harvesting. The ratio of tartaric acid to total free acid has the mean value of about 50 and 46 per cent., respectively, for musts of the 1930 and 1931 vintages, and is usually highest when the total acidity is lowest. On fermentation the quantity of tartaric acid was usually found to decrease in the 1930 musts, but at a rate which was independent of the amount of alcohol present, whilst in the latter any decreases were usually smaller and some increases are recorded. The data do not enable a reliable distinction to be drawn between the wines and vintage-years, and it is considered that the harvesting-date and storage-temperatures are also important factors. J. G.

Determination of Lactic Acid in Wines and Fruit Juices. L. Semichon and Flanzy. (*Ann. Falsificat*, 1932, **25**, 414–416.)—When lactic acid is oxidised in solution by potassium dichromate and sulphuric acid the CH.OH radicle separates as formaldehyde, which undergoes oxidation to carbon dioxide and water, and acetic acid remains. Of the compounds present in fruit juices or their fermented products, only lactic and pyruvic acids, higher fatty acids, and alcohols yield acetic acid under these conditions. The alcohols and the higher fatty acids are readily removable prior to the oxidation, and pyruvic acid has not been found in appreciable proportions in either fruit juices or wines. To determine the lactic acid, 50 c.c. of the liquid are boiled for an hour with excess of milk of lime under a reflux condenser, in order to saponify the esters. The liquid is then concentrated to one-half of its volume and the residue, when cold, is treated with excess of tartaric acid to liberate the acids. After the lapse of two hours, the mass is filtered into a 150- or 200-c.c. Kjeldahl flask, the residue on the filter being washed with a dozen quantities of a few c.c. of water; the total volume of the filtrate and washings should not exceed 50 c.c. Any remaining traces of alcohols and aldehydes, as well as the whole of the volatile fatty acids, are then removed by distillation in a current of steam, the flask being inclined at 45° and immersed in a boiling water-bath. Distillation is continued until the last 50 c.c. of distillate collected gives no indication of acidity with litmus. The residual liquid is then cooled and 1·5 grm. of chromic acid and 2 c.c. of sulphuric acid (sp.gr. 1·71) are added, the flask standing in cold water meanwhile. The contents of the flask are then heated, under a reflux condenser, on a steam-bath for an hour. The acetic acid is then distilled off in a current of steam, and is determined by titrating the distillate with lime water in presence of litmus; 1 molecule of acetic acid corresponds with 1 molecule of lactic acid.

When the wine contains more than 5 grms. of sugar per litre, the amount of oxidising solution used should be increased proportionally. If, during the oxidation, the liquid ceases to show a brown colour, the flask must be cooled and a fresh quantity of the oxidising mixture added. Traces of lactic acid may be carried over with the volatile fatty acids and may be determined in the distillate; it has, however, been found that such traces are negligible in amount.

T. H. P.

Determination of Succinic Acid in Wines and other Fermented Liquids. L. Semichon and Flanzy. (*Ann. Falsificat.*, 1932, **25**, 416–419.)—Of all the constituents of wine and of fermented liquors in general, only acetic and succinic acids are unattacked by the mixture of chromic and sulphuric acids used in the determination of lactic acid (preceding Abstract). Moreover, no constituent yields succinic acid on oxidation. The succinic acid may be determined as follows: A long-necked, 150- to 200-c.c. Kjeldahl flask, standing in cold water, is charged with 50 c.c. of the wine, 1·5 grm. of powdered chromic acid and 2 c.c. of sulphuric acid (sp.gr. 1·71), and is then heated for an hour in a boiling water-bath. The liquid is cooled and treated with ammonium hydrosulphide to reduce the excess of chromic acid, and afterwards with ammonia solution to precipitate chromium oxide. After being boiled until evolution of ammonia ceases, the liquid is filtered and the filter washed with water. The filtrate, containing ammonium sulphate and succinate, is concentrated—while kept stirred—to 1 c.c., and treated with 50 c.c. of 95 per cent. alcohol, which precipitates the whole of the sulphate. This is filtered off and washed with alcohol, the filtrate being distilled to recover the alcohol, and the liquid then evaporated to dryness. The residue of ammonium succinate is weighed; if it is not entirely free from sulphate, this is determined as barium sulphate, and the weight of the succinate corrected accordingly.

By combination of this method with that given for determining lactic acid (*loc. cit.*), one sample of wine may be used for the successive determinations of the total volatile fatty acids, lactic acid, and succinic acid. T. H. P.

Differentiation of Fermentation Vinegar from Artificial Vinegar. C. Bertin. (*Ann. Falsificat*, 1932, **25**, 412–413.)—Pastureau (ANALYST, 1905, **30**, 274) found that fermentation vinegar always contains methylacetol,

$$CH_3.CO.CH(OH).CH_3,$$

and Denigès (*Précis de Chimie Analytique*, 1931, Vol. II, 307) gives a method, based on the reduction of Fehling's solution, for detecting this compound in vinegar. This method is not very exact, but may be made quantitative by modifying it as follows:—Fifty c.c. of the vinegar are neutralised with anhydrous sodium carbonate, and then distilled, exactly 20 c.c. of distillate being collected. The distillate is poured into a mixture of 10 c.c. of copper sulphate solution (40 grms. of $CuSO_4$ and 1 c.c. of H_2SO_4 per litre), 10 c.c. of alkaline Rochelle salt solution (200 grms. of the salt and 150 grms. of NaOH per litre) and 5 c.c. of potassium ferrocyanide solution (50 grms. per litre). The mixture is heated to boiling, and the volume (*e.g.* 11·4 c.c.) of a standard solution of pure dextrose (*e.g.* 3·5 grms. per litre) necessary to reduce the whole of the copper salt present is determined. If the volume of the dextrose solution required for the reduction, under similar conditions, of the mixed copper solution in absence of the vinegar distillate is 13·0 c.c., the amount of methylacetol contained in 1 litre of the vinegar will be 0·112 grm. (expressed as dextrose). [The result given in the original, *viz.* 0·0112 grm. per litre, has been wrongly calculated.—*Abstractor.*] This procedure neglects any methylacetol which may not have distilled over. T. H. P.

Differentiation of Wine Vinegar from Spirit Vinegar. P. Rudolp and H. Barsch. (*Z. Unters. Lebensm.*, 1932, **64**, 293–295.)—A method of differentiating wine vinegar and spirit vinegar is based upon the fact that iodine is decolorised more rapidly by the reducing substances in the former than by those in the latter. (1) To 10 c.c. of the sample 0·5 c.c. of a 0·02 solution of iodine is added, and, after 15 minutes at 50° to 60° C., the mixture is cooled and 10 drops of a 1 per cent. solution of starch are added. In the presence of less than 5 per cent. of wine vinegar a deep blue colour is obtained, but more reduces the iodine so that the final colour is pale blue to bluish-green, or, if more than 20 per cent. is present, the liquid is colourless. If an excess of iodine solution is added and the mixture is back-titrated with 0·02 *N* sodium thiosulphate solution, the method may be made roughly quantitative. (2) The sample (100 c.c.) is decolorised in the cold with 2 grms. of animal charcoal, and 10 drops of a dilute solution of ferric chloride are added to 10 c.c. of the filtrate. Wine vinegar (more than 10 per cent.) appears yellow-green and spirit vinegar red to yellowish-red, but, as the latter colour also turns yellow on exposure to air, the colour should be estimated within 15 minutes. (3) A mixture of 10 c.c. each of the sample and of a reagent prepared from equal volumes of an ammoniacal solution of ammonium molybdate and 30 per cent. nitric acid gives a precipitate changing, through green, to an intense blue (MoO_2) in the presence of wine vinegar, whilst spirit vinegar produces a pale yellow-green shade. J. G.

Determination of Essential Oils in Drugs and Spices. T. T. Cocking and G. Middleton. (*Pharm. J.*, 1932, **129**, 253–255.)—The apparatus described provides a method of determining the amount of essential oil which may be distilled from a drug, not necessarily the amount contained in the drug. The measuring tube is of such a bore that 1 c.c. corresponds with a length of about 14 cm., and it has a small bulb at the bottom with a capacity of 0·9 c.c., and widens below towards the receiver, in which the oil separates from the aqueous distillate; this may be connected by means of a two-way stop-cock, either with the return-flow tube or with a side-tube through which it may be filled with distilled water. A narrow side-tube with a ground-in stopper between the condenser and measuring-tube serves as a vent. About 300 c.c. of water and a suitable quantity of drug are placed in the flask; the receiver is filled with distilled water from the side-tube, the tap is turned so that the return-tube is filled with water, the stopper is inserted in the vent-tube with a slip of paper under its seating, and the contents of the flask are boiled at such a rate that the receiving-tube does not become warm. Distillation is continued for about 2 hours, and, after the apparatus has drained, distilled water is made to enter the receiver very slowly to raise the layer of oil to the measuring tube. Distillation is continued for another hour, and the distillate is again measured. Oil of turpentine is used as a solvent for oils heavier than water, or for those which crystallise at the ordinary temperature. D. G. H.

Copper Content of Certain Pharmaceutical Preparations and Chemicals. N. Evers and L. A. Haddock. (*Pharm. J.*, 1932, **129**, 247–248.)—The proportions of copper (as parts per million) present in various chemical galenicals and miscellaneous substances are tabulated. The determinations were made by the authors' method as described in THE ANALYST (1932, 495), and the figures for various chemicals ranged from 0·4 in hydrochloric acid to 68 parts per million in ferric glycerophosphate, and in certain galenicals, etc., from 4 parts per million for tinct. valerian. ammon. B.P. to 580 for an ext. ergot., B.P. (1914). D. G. H.

Comparison of Tests for Balsam of Peru. E. M. Smelt. (*Pharm. J.*, 1932, 129, 241.)—The following tests are recommended for the detection of most of the adulterants reported to be used in balsam of Peru. (1) *Odour of the petroleum spirit extract.*—Three grms. of balsam are shaken with 15 ml. of petroleum spirit (boiling below 40° C.), and, after filtration if necessary, the solution is evaporated. No odour of turpentine or benzaldehyde should be apparent, whilst the presence of copaiba or Canada balsam may be suggested.

(2) *Acetic anhydride test.*—Three drops of the residue from (1) are dissolved in 10 drops of acetic anhydride and 2 drops of sulphuric acid are added. If there is no reddish-violet or bluish-violet colour, the absence of Canada balsam, copaiba, colophony, gurjun balsam and storax is indicated.

(3) *Nitric acid test.*—To 4 drops of residue from (1), 2 drops of nitric acid are added, when if a yellow but not green, blue, or purplish-red colour develops round the drops, the absence of balsam of tolu, Canada balsam, copaiba, colophony, gurjun balsam, storax, turpentine, castor or olive oil is indicated.

(4) *Copper acetate test.*—Four ml. of the petroleum spirit solution from (1) are shaken with 10 ml. of a 0·1 per cent. w/v aqueous solution of copper acetate and left to separate. The petroleum spirit layer is not coloured green in the absence of Canada balsam, copaiba, or colophony.

(5) *Alcohol test.*—One volume is soluble in 1 volume of 90 per cent. alcohol, but, on further addition of 2 or more vols. of alcohol, the solution becomes turbid. Artificial balsams, the ingredients of which are completely soluble in 90 per cent. alcohol, are thus detected.

(6) *Chloral hydrate test.*—One grm. of balsam is shaken with a solution of 3 grms. of chloral hydrate in 2 ml. of water, and if, after standing for 15 minutes, there is a clear solution, the absence of castor and olive oils is indicated.

(7) *Carbon disulphide test.*—If three volumes mixed with 1 volume of carbon disulphide give a clear solution, the absence of gurjun balsam (?) olive oil (?) and kerosene is indicated. D. G. H.

Merz Reactions for Certain New Anaesthetics. H. Szancer. (*J. Pharm. Chim.*, 1932, 124, 239–241.)—Merz divides the anaesthetics examined into two groups, the first containing the bases soluble only with difficulty (laracaine, percaine, and pantocaine), and the second group, consisting of novocaine, tutocaine, and psicaine. The diazo reaction, the iodoform reaction after saponification, and the addition to the free base (dissolved in ether) of an ethereal solution of oxalic acid, which may be used as reactions for novocaine and tutocaine, give negative results with psicaine. To identify this substance (which is a pseudococaine) Merck's reaction (*Prüfung der Spezialpräparate*, 1930, 3rd Ed.) may be employed. One grm. of psicaine is heated with 1 c.c. of concentrated sulphuric acid to 100° C., and 2 c.c. of water are added, when the odour of the methyl ester of benzoic acid becomes apparent. Cocaine, which gives a similar reaction, may be distinguished by such tests as those given in Hager's *Handbuch der pharmazeutischen Praxis.* D. G. H.

Quantitative Methods for the Determination of Theobromine in Diuretine. J. M. A. Hegland. (*Pharm. Weekblad*, 1932, **69**, 1078–1080.)—(1) A solution of 0·5 grm. of sample in 100 c.c. of water is made neutral to phenolphthalein, and is then shaken with excess of a 0·1 *N* solution of silver nitrate, the nitric acid liberated after 24 hours being titrated with 0·1 *N* sodium hydroxide solution to phenolphthalein; 1 c.c. ≡ 18 mgrms. of theobromine (H. Boie). (2) A mixture of a solution of 0·25 grm. of sample in 2 c.c. of glacial acetic acid with 50 c.c. of 0·1 *N* iodine solution, 6 grms. of sodium chloride and 5 c.c. of dilute hydrochloric acid is diluted to 100 c.c., and, after 24 hours, the theobromine tetraiodide is removed by filtration, and the excess of iodine in an aliquot portion of the filtrate is titrated with 0·1 *N* sodium thiosulphate solution; 1 c.c. of 0·1 *N* iodine solution ≡ 4·5 mgrms. of theobromine (Mahler and Schütz, after Emery and Spiner). A comparison of the results obtained by the two methods in the presence of sodium salicylate shows that (1) gives slightly high results, but is safer and less dependable on variations in conditions than (2), which gives low results.

J. G.

Colorimetric Assay of Ergot. N. L. Allport and T. T. Cocking. (*Pharm. J.*, 1932, **129**, 235–236.)—In order to eliminate, in the B.P. 1932 colorimetric test for the standardisation of ergot, the exposure to light of the alkaloidal solution with the *p*-di-methyl-amino-benzaldehyde and sulphuric acid reagent, ferric chloride was used as a catalyst. The reagent consisted of a 0·125 per cent. w/v solution of *p*-dimethyl-amino-benzaldehyde in sulphuric acid (65 per cent. v/v), to which 0·1 per cent. v/v of a 5 per cent. solution of ferric chloride was added, 2 ml. of this reagent being added to 1 ml. of the alkaloidal solution. The full colour is found to develop within 1 minute without exposure to light or further heating, and the reagent may be stored in the dark for about a month without losing its activity. Stress is laid on the importance of using pure anaesthetic ether for the extraction. Ten samples of ergot, liquid extract, percolate and paste were tested with the above reagent, and also by the official reagent, with warming to 45° C. and exposure to light, and the results obtained in the two series of tests were almost identical.

D. G. H.

Assay of Santonin-bearing Drugs. H. M. Burlage and A. C. Smith. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 491–499.)—Investigation of 17 methods which have been proposed for the determination of santonin has been made, 3 different samples of drugs being used. It was found that Feldhoff's (*Pharm. Z.*, 1925, **70**, 661) and Eder and Schneiter's methods (*Schweiz. Apoth.-Ztg.*, 1925, **63**, 405) gave uniform results and a product of satisfactory melting point, and seemed worth further study. The following modification of Feldhoff's procedure is suggested: chloroform is used in place of ether for extracting the drug and, later, instead of allowing the santonin to crystallise from 15 per cent. alcohol, the alcoholic solution is transferred to a 100-c.c. flask, mixed with 2·5 grms. of potassium hydroxide and, after 15 to 20 minutes, made up to 100 c.c. with 95 per cent. alcohol. A check determination is made with 2 grms. of santonin in the same way, the solution thus obtained being compared colorimetrically with that given by the drug.

A new method, which yields results in good agreement with those of the modified Feldhoff process, makes use of alcohol as the primary solvent, and is carried out as follows:—A weighed quantity of about 10 grms. of the finely powdered drug is boiled for 15 minutes with 50 c.c. of petroleum spirit (saturated with santonin) under a reflux condenser to de-fat the sample. The mixture is filtered by means of suction, and the drug extracted for 3 hours in an extraction thimble in a Soxhlet apparatus with 75 c.c. of alcohol. The extract is evaporated to 10 c.c. and filtered through a plug of cotton-wool, the flask and filter being washed with 25 c.c. of boiling water, and the liquid filtered again through paper into an Erlenmeyer flask. The flask and filter are then washed twice with 10-c.c. portions of hot 15 per cent. (by vol.) alcohol. The filtrate is boiled with 1·5 to 3 c.c. of lead subacetate solution (U.S.P., X, 221), and filtered hot through a plain filter into a tared Erlenmeyer flask, the boiling flask and the filter being washed with two 10 c.c.-portions of hot 15 per cent. (by vol.) alcohol. The filtrate is left for 24 hours in a cool, dark place, and its weight determined. The separated crystals are transferred to a tared filter, and the flask and filter are washed thrice with small quantities of 5 per cent. ammonia solution and thrice with water. The crystals of santonin are dried at 100° C. until of constant weight, this being increased by 0·006 grm. for each 10 grms. of the weighed dilute alcohol solution. T. H. P.

Assay of Santonin in *Artemisia*. J. Coutts. (*Pharm. J.*, 1932, **129**, 240–241.)—The following gravimetric method of assay of santonin in *Artemisia* is applicable to the various types of the drug, and gives results comparable with those obtained by the methods of Katz, Fromme and Mouton. Fourteen grms. of the dried, coarsely powdered drug are shaken at frequent intervals for 6 hours with 140 ml. of benzene; 101 ml. of the liquid are filtered off and shaken for 5 minutes with 35 ml. of 8 per cent. sodium carbonate solution. After separation, 80·5 ml. of the benzene solution (8 grms. of the drug) are decanted and evaporated to dryness. The residue is extracted by heating it for 10 minutes with 60 ml. of saturated barium hydroxide solution at 95° C., and the solution is immediately filtered, and the residue is washed with two 10-ml. portions of the hot barium hydroxide solution. The solution is allowed to cool, slightly acidified with 5 ml. of 25 per cent. hydrochloric acid, and left to crystallise for 24 hours. The crystals are collected and washed with cold water, dried and weighed, the weight representing the santonin found in 8 grms. of the crude drug. The benzene used should be completely volatile below 95° C. D. G. H.

Detection of Solanine. B. Alberti. (*Z. Unters. Lebensm.*, 1932, **64**, 260–262.)—The usual alkaloid separation is carried out, and a solution of the resulting residue in 1 drop of glacial acetic acid is mixed with 2 drops of concentrated sulphuric acid, and 1 drop of a 1 per cent. solution of formaldehyde (or of 0·5 per cent. hydrogen peroxide) is then added. In the presence of more than 0·0025 to 0·005 mgrm. of solanine or of solanidine a stable cherry or purple-red colour is obtained which deepens on standing (Autenrieth's selenium reagent is sensitive to 0·025 mgrm.). Quillaia or senega saponins, and narcotine, narceine, thebaine, caffeine, strychnine, brucine, digitalin or digitonin do not interfere; morphine gives the reaction with formaldehyde, but none with hydrogen peroxide. Potato-skins are extracted in the cold with glacial acetic acid. Concentrated sulphuric acid is coloured yellow by solanine. J. G.

Appearance of Nicotine in Cigarette Smoke. II. C. Pyriki. (*Z. Unters. Lebensm.*, 1932, **64**, 263–277.)—Modifications of Pfyl and Schmitt's method (ANALYST, 1927, **52**, 728) for the determination of nicotine in tobacco-smoke (*cf. id.*, 1931, **56**, 753; Barta and Toole, *Z. angew. Chem.*, 1931, **44**, 682; Kaperina, *Biochem. Zeit.*, 1930, **219**, 258) are criticised and rejected. The author prefers to extract the acid-absorbing solution with chloroform and to neutralise the aqueous portion before precipitation with picric acid or iodoeosin, the slightly higher results thus obtained being attributed to the inclusion of a higher proportion of decomposition-products. No nicotine is detectable in this way in the smoke from tobaccos containing less than 0·2 per cent. of nicotine; tobaccos containing 0·3 and 0·5 per cent. yield about 5 and 12·5 per cent. of these quantities, respectively, but when they contain 1·2 per cent. or over (up to 2 per cent.) the yield is always about 20 per cent. A number of denicotinising agents (*cf. Z. angew. Chem.*, 1931, **44**, 881; *D.R.P.*, 518,903; and *Pharm. Zentralh.*, 1932, 73, 257) were examined, and found to be without effect, and, in particular, "Bonicot" (*Chem. Ztg.*, 1932, **56**, 31), which reduces the nicotine content by about 13 per cent., was found to be no better than water, and probably acts by making the tobacco moist. The author's work confirms his previous suggestions (ANALYST, 1931, *loc. cit.*) for the nicotine-contents of tobaccos marked "nicotine-free" and "poor in nicotine," and indicates that the nicotine is carried over in the smoke in loose combination with acid decomposition-products. If 75 per cent. of a cigarette is smoked, the nicotine-content of the residue is increased by 11 to 13 per cent. J. G.

Polarimetric Method for the Determination of Calcium Gluconate. H. J. Fisher and E. M. Bailey. (*J. Assoc. Off. Agr. Chem.*, 1932, **15**, 461–466.)—This method is based on the observations that uranium salts considerably enhance the optical rotation of solutions of calcium gluconate, and that, when the solutions are saturated with uranyl acetate, the rotations are a linear function of the concentration of the gluconate, provided this is not high. The presence of sugars in proportions likely to occur in commercial preparations of calcium gluconate does not affect the results appreciably. The calcium gluconate tablets now being sold are chocolate-flavoured, this necessitating slight modification of the procedure. Calcium lactate causes no interference.

Two 0·5 grm.-portions of the calcium gluconate or, with tablets containing 50 per cent. or less of the salt, two 1 grm.-portions are weighed. If chocolate or a fatty base is present, the samples are washed several times on a hardened filter with absolute ether, and the residues are warmed until the ether is expelled. Each portion is warmed with 20 c.c. of water in a 25 c.c.-measuring flask until the calcium salt present is dissolved. To one flask 5 grms. of powdered uranyl acetate are added, the flask being stoppered and shaken in a machine for an hour, during which time the other flask remains untreated. If the sample contains chocolate, a little alumina cream is added to each flask, and both are cooled to 20° C. The contents of each flask are made up to volume, with saturated uranyl acetate solution for the flask to which this acetate was added, and with water for the other. Each solution is filtered and polarised in a 200 mm. tube, white light being used. If A is the rotation in degrees Ventzke of the solution free from uranyl acetate and B that of the other solution, the percentage of monohydrated calcium gluconate is 4·3 $(B-A)$ if 1 grm. of sample were taken, or double this if 0·5 grm. were used.

The accuracy with which the rotation of solutions can be read in an ordinary saccharimeter is a limiting factor in the accuracy obtainable by this method, and for the pure salt or mixtures containing no calcium compounds other than the gluconate, determination of the calcium by the permanganate method is doubtless preferable. The polarimetric method, although of a lower degree of accuracy, is the only known method applicable either to identification of the gluconate or to its determination in mixtures containing other calcium salts. The presence of tartrates and active malates would interfere with the method, but the low solubilities of calcium tartrate and malate would prevent substitution of these salts for the gluconate. Active calcium lactate is not a commercial product. T. H. P.

Determination of Titanium in Pomades. E. Kahane. (*J. Pharm. Chim.*, 1932, **16**, 194–202.)—Titanium dioxide is stated to replace zinc oxide, partly or completely, in certain ointments, cosmetic creams, etc. The following method for the determination of the titanium was found suitable.

Destruction of Organic Matter.—Two grms. of the material are introduced into a Kjeldahl flask and 4 grms. of anhydrous sodium sulphate, 10 c.c. of concentrated sulphuric acid, and 5 c.c. of concentrated nitric acid are added. The whole is heated, and, when blackening occurs, a few drops of a mixture of 2 volumes of perchloric acid (sp.gr. 1·6) and 1 volume of concentrated nitric acid are added, from time to time, until no blackening is produced on further heating. The liquid is finally boiled for a few minutes to ensure that the titanium dioxide is dissolved.

Gravimetric Determination of Titanium.—Fifty c.c. of water are added to the contents of the flask; the liquid is filtered, neutralised with sodium carbonate solution, then acidified with 1 c.c. of concentrated sulphuric acid, and 6 grms. of sodium thiosulphate are dissolved in it. The solution is added, little by little, to 400 c.c. of boiling water kept constantly stirred during the addition; the boiling is continued for 2 minutes, and the liquid is then cooled rapidly in cold water. The precipitate, consisting of a mixture of titanium hydroxide and sulphur, is filtered off, washed with boiling water, ignited and weighed as TiO_2. This method is said to give good results in the presence of the iron and zinc which may occur in the sample, but other metals which precipitate under the conditions used (bismuth, for example) must, if present, be removed by preliminary separation. Details are given for alternative volumetric and colorimetric determinations, which follow established methods. S. G. C.

Biochemical

Determination of Methionine in Proteins. H. D. Baernstein. (*J. Biol. Chem.*, **1932**, **97**, **663–668**.)—A modification of the technique of Pollak and Spitzer (*Monatsh. Chem.*, 1922, **43**, 113) is described for the determination of the volatile iodide arising from proteins treated with hydriodic acid. Their observation that the precipitate in the absorber is not all silver iodide, since a portion may be dissolved in nitric acid, is confirmed. When this portion is reprecipitated as silver iodide the combined weight is equivalent to the methionine taken. The tedious treatment of the precipitate is eliminated by a volumetric determination of the silver remaining in the filtrate from the silver iodide precipitate. The modified method is as follows:—About 0·5 grm. of protein is weighed and transferred to a digestion flask, and a small piece of porcelain is added to insure quiet boiling. Ten c.c. of pure hydriodic acid (sp.gr. 1·7) are added, and the flask is connected with a condenser to which one wash-bottle and two absorbers are attached. A figure shows the apparatus. The wash-bottle contains 20 per cent. cadmium sulphate solution acidified with sulphuric acid and with 1 c.c. of red phosphorus suspension added. This removes any hydrogen sulphide, iodine and hydriodic acid which might come over from the flask. The absorbers contain 10 c.c. of a solution of silver nitrate in absolute alcohol. To prepare this solution, 500 c.c. of absolute alcohol and 8 grms. of silver nitrate are boiled beneath a reflux condenser for half-an-hour, and the solution is left to stand in the sunlight for two days, then filtered through very fine paper, and kept in a brown bottle. Washed carbon dioxide is bubbled through the apparatus under a pressure of about 2 pounds. (The gas is washed with silver nitrate and sulphuric acid.) The rate of bubbling is regulated by a screw clamp on the inlet to the flask. The mixture in the flask is brought to boiling with a small flame, and the rate of outflow of gas is then regulated by a second screw clamp between the wash-bottle and first absorber. The bubbling should be just so fast that the bubbles can be counted. Water at about 60° C. is run through the condenser jacket. About 90 per cent. of the methyl iodide comes over in the first hour; the remainder takes several hours more. The author allows the apparatus to run all night (about 15 hours). The absorbers are rinsed carefully into 50-c.c. beakers, which are heated on the water-bath until the volume is reduced to about 10 c.c. The solution is transferred to a 50-c.c. flask, diluted to the mark, and filtered, and 5·0 c.c. of the filtrate are titrated with 0·02 *N* potassium thiocyanate solution, after the addition of 2 c.c. of nitric acid and 2 c.c. of saturated ferric alum solution, a micro-burette being used. A blank determination is made without the protein, and the difference gives the amount of silver iodide precipitated by the methyl iodide derived from the protein. The method gives nearly theoretical figures (97·6 ± 1·4 per cent.) with pure synthetic methionine. The methionine-content of proteins thus determined ranges from 0·5 to 5·0 per cent. Certain difficulties of interpretation are discussed. Eleven amino acids analysed by the new technique gave negative results. No one has yet isolated an amino acid containing the methoxyl group, and, excepting methionine, none of the amino acids tried by the author (which include representatives of each of the various classes of amino acids), yields a volatile iodide under the conditions described. The author believes that the methyl iodide liberated is a measure of the methionine only. P. H. P.

Mode of Distribution of Glucose in Human Blood. E. M. MacKay. (*J. Biol. Chem.*, **1932, 97,** 685–689.)—Glucose, so far as is known, readily permeates the red blood-cells, and there is no reason to suppose that the conditions which determine the distribution of electrolytes on the two sides of the erythrocyte "membrane" would influence its distribution, so that it is reasonable to believe that the concentration of glucose in the plasma and erythrocytes would be in accordance with the aqueous concentrations of these media. The author has made experiments on this point, since it has not been directly considered in the literature. A table shows the results obtained with 15 specimens of venous blood drawn both from normal and pathological subjects. It is shown that glucose is found in the same concentration in the water contained in the plasma and erythrocytes of freshly-drawn human blood; it is also found equally distributed between the plasma and cell water after the addition of glucose to human blood *in vitro*. The distribution of glucose between the erythrocytes and plasma is apparently, therefore, a process of simple diffusion, and is governed by the aqueous concentrations of these two media. P. H. P.

Determination of Magnesium in Blood by means of 8-Hydroxyquinoline. D. M. Greenberg and M. A. Mackey. (*J. Biol. Chem.*, 1932, **96**, 419–429.)—A method is described for the determination of magnesium in oxalated whole blood, oxalated plasma, and serum. The magnesium determination is carried out on a protein-free blood filtrate, prepared either by a modification of the Folin-Wu or the trichloroacetic acid method, and in a dilution of 1:5 so that 5 c.c. of filtrate represent 1 c.c. of blood. Equations show the reactions involved. Magnesium hydroxyquinolate is formed in an ammoniacal solution. The hydroxyquinoline reacts with bromine formed by the reaction of bromate with an excess of bromide in acid solution. More bromate is added than is actually required to brominate the hydroxyquinoline, and the excess is determined iodimetrically by the addition of potassium iodide to the solution to react with the excess of bromate and titration of the liberated iodine. The following reagents are required: *For the preparation of the blood filtrates*, a 10 per cent. sodium tungstate (Na_2WO_4) solution and 0·67 *N* sulphuric acid for the modified Folin-Wu, 10 per cent. trichloroacetic acid for the trichloroacetic acid filtrate, and 4·5 per cent. neutral potassium oxalate solution to precipitate calcium in serum. *To precipitate and wash the magnesium hydroxyquinolate*, 1 per cent. 8-hydroxyquinoline solution in 95 per cent. ethyl alcohol (freshly made every 2 weeks), 1 per cent. ammonium chloride solution, concentrated ammonium hydroxide, a 2 per cent. ammonium hydroxide wash solution, and 95 per cent. ethyl alcohol. *For the titration*, concentrated hydrochloric acid, 50 per cent. potassium bromide, exactly standardised 0·01 *M* potassium bromate, 20 per cent. potassium iodide, 1 per cent. soluble starch, and approximately 0·1 *N* sodium thiosulphate solutions. For the potassium bromate solution 1·670 grm. of the pure dry crystalline salt is dissolved in 1 litre of water at room temperature. For the filtration, a battery of Kirk-Schmidt micro-filters fitted into 250-c.c. Pyrex suction filtration flasks is used. Filters with stems 2 inches long were found most suitable.

Procedure for oxalated whole blood or plasma: Sufficient neutral sodium or potassium oxalate is added to the blood for it to contain about 0·4 per cent. of oxalate; this precipitates the calcium. By the Folin-Wu method a protein-free filtrate is prepared from the oxalated whole blood or plasma by the addition to one volume of blood of 2 volumes of distilled water, then 1 volume of 10 per cent. sodium tungstate solution, and finally slowly, with shaking, 1 volume of 0·67 *N* sulphuric acid. After addition of the distilled water to whole blood the sample is shaken, and left until the corpuscles have been haemolysed. Addition of a drop of concentrated ammonia to samples that haemolyse with difficulty is helpful. The coagulum is left for 15 minutes or longer, and then filtered or centrifuged off. This gives a completely protein-free filtrate. A trichloroacetic acid filtrate is prepared by the addition of 2 volumes of distilled water to 1 volume of blood; then, after whole blood has been laked, 2 volumes of 10 per cent. trichloroacetic acid are added to coagulate the protein. When a single determination is to be made on a sample, 3 c.c. of blood or plasma are pipetted into a test-tube fitting into a 15-c.c. centrifuge holder, then 6 c.c. of water and 3 c.c. each of sodium tungstate and sulphuric acid, or, alternatively, 6 c.c. of trichloroacetic acid. After standing, the tube is centrifuged, and a 10-c.c. portion of the supernatant liquid is pipetted off for analysis. The 10-c.c. aliquot portion (equivalent to 2 c.c. of the original blood or plasma) of the protein-free filtrate is introduced into a 15-c.c. test-tube, 1 c.c. of 1 per cent. ammonium chloride solution is added, then 6 drops of concentrated ammonium hydroxide, followed by 1 c.c. of the 1 per cent. alcoholic hydroxyquinoline solution. For trichloroacetic acid filtrates the concentrated ammonia added is insufficient for neutralisation, and this can be detected by the green tint of the liquid. More ammonia is added, drop by drop, until the hydroxyquinoline colour in the tube changes to yellow. The contents are mixed, and the tube is placed for 20 to 30 minutes in a water-bath maintained at 70° to 80° C. While the solution is still hot it is filtered through a Kirk and Schmidt micro-filter, gentle suction being used. The precipitate is washed first with 8 c.c. of hot 2 per cent. ammonium hydroxide, then with 8 c.c. of 95 per cent. ethyl alcohol, and finally with another 8-c.c. portion of hot 2 per cent. ammonium hydroxide with the aid of suction, and the filter is then transferred to a clean filter-flask, and treated with 8 c.c. of hot concentrated hydrochloric acid to dissolve the magnesium precipitate; finally, the filter-cup is washed out with water. The titration is carried out in the filter-flask. To the contents 1 c.c. of 50 per cent. potassium bromide is added, then slowly, with a calibrated pipette, 5 c.c. of 0·01 *M* standard potassium bromate solution. The whole is gently shaken for 1 minute to allow of the bromination of the hydroxyquinoline, after which 1 c.c. of 20 per cent. potassium iodide solution is added. The flask is again shaken, and its sides are washed down with water to give a volume of about 50 c.c. To titrate the excess of iodine with thiosulphate, 0·02 *N* sodium thiosulphate is used, 10 c.c. being added from a calibrated pipette, and the rest of the titration being continued with a micro-burette calibrated in 0·02 c.c. The titration is first carried to a pale straw-colour, then 20 drops of 1 per cent. starch solution are added, and the titration is continued to the disappearance of the blue colour. The accuracy of the method depends upon the standardisation of the bromate solution. The strength of the thiosulphate is determined in each series of analyses by a blank titration as follows: Into an Erlenmeyer flask of 200 to 300-c.c. capacity, 8 c.c. of concentrated hydrochloric acid are introduced, followed by 8 c.c. of water and 1 c.c. of 50 per cent. potassium bromide solution. These are mixed, and the same volume of standard bromate is pipetted in as for the magnesium determinations. The flask is gently shaken for 1 minute, 1 c.c. of the 20 per cent. potassium iodide solution is added, and the sides are washed down, as before, to give a volume of about 50 c.c. The titration is made with pipette and burette, and the differences between that of the blank and those of the magnesium samples give the amounts used up in the bromination. *Procedure for serum*: This depends upon whether or not calcium needs to be determined. If not, 3 c.c. of serum and 5 c.c. of water are placed in a tube, followed by 3 c.c. of 10 per cent. sodium tungstate solution, and 3 c.c. of 0·67 *N* sulphuric acid are added slowly, with shaking. After 5 minutes, 1 c.c. of 4·5 per cent. potassium oxalate solution is added, and the whole is left for 2 hours. The tube is then centrifuged and a 10-c.c. aliquot part of the filtrate (representing a 2-c.c. aliquot part of serum) is taken for analysis, which is carried out as described for plasma. When calcium is to be determined, the filtrate is prepared as for whole blood. Some results of typical experiments showing the accuracy of the analytical method for magnesium and calcium are given.

P. H. P.

Variations in the Vitamin *A* Content of Butter-Fat. G. S. Fraps and R. Treichler. (*Ind. Eng. Chem.*, 1932, 24, 1079–1081.)—Butter fat from cows receiving maize, cotton-seed meal and pasturage contains from 17 to 50 units (U.S.P.) of vitamin *A* per grm., and the content remains high even in dry weather with shortage of grass. After sixteen months' feeding with cotton-seed meal and husks, cows yield butter-fat containing 2 units (U.S.P.) of vitamin *A* per grm.; with the addition of silage to the feed, the vitamin content is 2 to 16 units (U.S.P.) per grm., and rises to about 33 units when the cows have also access to pasturage. Only a small fraction of the vitamin contained in any of the feed is found in the butter-fat.

W. P. S.

Halibut-liver Oil. Its Vitamin Potency, Physical Constants and Tolerance. A. D. Emmett and O. D. Bird. (*Ind. Eng. Chem.*, 1932, 24, 1073–1077.)—Halibut-liver oil has the following characteristics: Sp.gr. at 25° C., 0·927 to 0·928; unsaponifiable matter, 7·44 to 7·90 per cent.; saponification value, 179 to 193; iodine value, 118 to 126. The vitamin *A* potency of the oil varies from 37,500 to 62,500 units, or from 75 to 125 times that of cod-liver oil. The vitamin *D* potency of the oil is also much greater than that of cod-liver oil. The tolerance to large quantities of halibut-liver oil indicates that it can be taken with impunity and accepted as a valuable accessory to human nutrition. W. P. S.

Bacteriological

Thermophilic Bacteria in Refined Cane Sugars. W. L. Owen and R. L. Mobley. (*Ind. Eng. Chem.*, 1932, 24, 1042–1044.)—Even the highest grades of refined sugars are frequently contaminated by the presence of thermophilic bacteria, and the use of such contaminated sugars is a source of trouble in the canning industry. The spores appear to be confined entirely to the surface of the crystals, and the infection is mainly derived from the dust of the factory, and sacks. The following summarised data illustrate the results obtained with various grades of sugars from many different sources:

Grade of sugar	Average flat, sour thermophiles per 10 grms.	Percentage free from flat, sour thermophiles	Percentage having anaerobes	Percentage containing H_2S-producers
Fine granulated ..	13·00	39·0	14·0	12
Coarse granulated ..	8·5	10·0	33	10
Powdered	191·0	0	50	50
Raw	70·0	0	28	0
Sacks	5·5 sq. in.	40 (infected)		

W. P. S.

Agricultural

Determination of Catalase in Agricultural Products. A. K. Balls and W. S. Hale. (*J. Assoc. Off. Agr. Chem.*, 1932, **15**, 483–490.)—The determination of catalase activity in agricultural products is beset by many difficulties, but the method described is satisfactory in so far that, with mixtures of clover and grain extracts, it yields additive results. Under the conditions specified the course of the catalytic reaction is unimolecular, and the constant is proportional to the amount of enzyme preparation used, but, owing to the fact that many factors seem to modify the results, this is not regarded as a proof that the true course of catalase reaction is unimolecular.

To prepare the enzyme material, 2 grms. of the substance are ground with sharp sand and 18 c.c. (20 c.c. if the substance is dry) of a mixture of 95 per cent. glycerol and 0·2 *M* phosphate buffer (p_H = 7·0 to 7·2); it is best first to remove the air from the extraction fluid by boiling it for a short time in a vacuum. The grinding is continued for several minutes until the material is very finely divided, the resulting emulsion is centrifuged, and the supernatant liquid is again freed from air. A suitable quantity of the liquid is then allowed to stand for 5 minutes with one-tenth of its volume of boiled liver-juice (*vide infra*) and, if necessary, afterwards diluted with more glycerol and phosphate mixture prior to introducing a measured quantity (1 to 5 c.c.) into the hydrogen peroxide solution for the analysis. The amount of enzyme used should be sufficient to decompose at least one-half of the peroxide in 5 to 7 minutes. It is added from a measuring pipette into a stoppered cylinder containing 1 c.c. of 0·2 *N* hydrogen peroxide solution (*vide infra*), 4 to 6 c.c. of 0·2 *M* phosphate buffer (p_H = 7·0), and approximately 1 grm. of freshly-dissolved dextrose in sufficient water to make, with the enzyme solution, a total volume of 50 c.c.; the cylinder and its contents must have been previously cooled in ice. The cylinder is replaced in the ice and, as soon as convenient, a 10 c.c. portion is rapidly pipetted into a flask containing 20 c.c. of 2 *N* sulphuric acid and 5 drops of saturated aqueous molybdic acid solution. Ten c.c. of 10 per cent. potassium iodide solution are added at once, and the liquid is left for 4 minutes, the iodine liberated being then titrated with 0·01 *N* thiosulphate solution.

Another 10-c.c. portion is removed after about 2 minutes, and a third after about 5 minutes, the moment when the delivery pipette is half empty being noted by a stop-watch in each case. The first titration gives the initial concentration of the peroxide (a) and the subsequent ones the amounts of peroxide remaining ($a - x$) at the time of observation (t). Substitution in the formula $\frac{1}{t} \log \frac{a}{a-x} = k$ gives the constant, which varies with the amount of enzyme and serves as a direct measure of it. The value thus obtained may also be calculated back to the dry weight of the enzyme preparation (corresponding with the 10-c.c. portion), and thus to the catalase factor, which is the k units per grm. of dried material. Slight variations in the concentration of the hydrogen peroxide solution do not affect the results, and exact standardisation of the thiosulphate and peroxide is unnecessary. The method gives results agreeing to within about 10 per cent.

To prepare liver-juice, fresh liver is ground and mixed with approximately five times its weight of water, the liquid portion being removed and treated with about 1 per cent. of its volume of 0·1 N iodine; the mixture should not show free iodine. The liquid is heated rapidly to boiling and filtered, the filtered extract being quickly cooled. This extract retains its activity for several weeks if covered with toluene and kept cool. The hydrogen peroxide used must be free from stabilising preservatives and may be prepared by adding, gradually and with stirring, 7·8 grms. of the purest sodium peroxide to 1 litre of water containing 54·4 grms. of pure potassium dihydrogen phosphate and cooled to 0° to 2°. Practically no oxygen is evolved, and, after the sodium peroxide is dissolved, the solution should have p_H 7·0 to 7·1, and contains 0·2 N hydrogen peroxide and 0·2 M phosphate buffer. At a low temperature this stock solution keeps well.

T. H. P.

Organic Analysis

Determination of Primary Propyl Alcohol in Mixtures of Ethyl Alcohol and Water. O. Noetzel. (*Z. Unters. Lebensm.*, 1932, **64**, 288–293.)—Values for n (determined by the dipping and Abbé refractometers) and sp.gr. of mixtures containing 60 per cent. of water, and 0 to 40 per cent. of n-propyl or ethyl alcohol, or both, are tabulated, and enable the proportion of the former to be determined, although the method does not distinguish it from *iso*-propyl alcohol. The following chemical method was selected after comparisons of the various colour reactions of the oxidation-products of these alcohols:—Five c.c. of the sample, which should be a distillate and should contain about 40 per cent. of total alcohols (*i.e.* sp.gr. 0·95), are placed in a 200-c.c. round-bottomed flask with 6 c.c. of a 25 per cent. solution of chromic acid, 0·5 c.c. of 50 per cent. sulphuric acid and a little pumice, and the mixture is then distilled through a delivery tube, 10 mm. wide, connected with a vertical condenser (*i.e.* similar to a Reichert–Meissl apparatus, but without the bulb). The outlet, which should be pointed, dips into a test-tube marked at 4 c.c. and immersed in ice-water, and the distillation (of 4 c.c.) should be complete in 5 minutes. Exactly 3 drops of a 2 per cent. solution of vanillin in alcohol and 4 c.c. of fuming hydrochloric acid are shaken with 0·6 c.c. of distillate, and, after 6 minutes at 65° C., the mixture is cooled, diluted if necessary with 4 to 8 c.c. of 25 per cent. hydrochloric acid, and the colour is then matched against that from a suitable alcohol mixture treated in the same way, or against a colloidal solution of copper ferrocyanide. An orange colour indicates 3 per cent. of *n*-propyl alcohol, rose 5, red-brown 10, purple-red to brown 15, and deep purple 20. The accuracy is 3 per cent., and the reaction is unaffected by small amounts of *iso*-propyl alcohol; *n*-butyl alcohol gives a similar colour, but may be distinguished by its different physical constants. J. G.

Detection of Acetone by means of *o*-Nitrobenzaldehyde. R. Raw. (*J. Soc. Chem. Ind.*, 1932, **51**, 276T.)—The aqueous solution to be tested is mixed with three volumes of acetone-free methyl or ethyl alcohol and heated to boiling with a few crystals of *o*-nitrobenzaldehyde for about one minute. It is then poured into an equal volume of 10 per cent. sodium hydroxide solution and again heated for a few minutes at 80° to 90° C. In the presence of acetone a precipitate of indigotin appears almost immediately. If the amount is small, the solution should be allowed to stand overnight, the precipitate then settling to the bottom of the tube. The test is specific for acetone. R. F. I.

Analytical Classification of the Fish-Liver Oils. N. Evers and W. Smith. (*Pharm. J.*, 1932, **129**, 234–235.)—For the purpose of classification the iodine value of the unsaponifiable matter and the acid phthalic ester value are regarded as the most important to be determined in the case of fish-liver oils, which, commercially, fall into three groups; those of the *Gadidae* family (cod, haddock, etc.), those of the *Elasmobranchae* (shark, dog-fish, skate), and those of a few miscellaneous fish such as hake and halibut. Analytical data are given for a number of authenticated liver oils, and it is pointed out that the difficulty of extracting the whole of the unsaponifiable matter accounts for many of the low published figures. A table is given of mean values and limits for the ordinary tests for a large number of cod-liver oils. Determination of the cholesterol of the unsaponifiable matter groups the oils roughly into their zoological classification. The bulk of the cholesterol is separated in crystalline form by dissolving the unsaponifiable matter in about 10 volumes of absolute methyl alcohol, leaving the solution for 24 hours at 0° C., and filtering off the crystals. The methyl alcohol is evaporated, the residue is dissolved in about 10 volumes of acetone, and any insoluble matter is filtered off after 24 hours. Oils of the *Gadidae* family have definitely higher iodine values than any of the others (except those shark-liver oils containing large amounts of squalene). D. G. H.

The Yellowing of Oxidised Drying Oils. A. C. Elm and G. W. Standen. (*Ind. Eng. Chem.*, 1932, **24**, 1044–1045.)—Examination of the transmission spectra of alcoholic solutions of ketohydroxy- and diketostearic acids showed that the yellowing of oxidised drying oils is not due to the presence or formation of ketohydroxy compounds in the oil film. Diketostearic acid is yellow, whilst ketohydroxy stearic acid is colourless. The former has a well-defined absorption band in the blue end of the spectrum, whilst the latter has a less pronounced selective absorption, which, however, is entirely located in the ultra-violet region, and, therefore, cannot produce colour. Even the addition of excess of alkali does not produce a coloured compound. W. P. S.

Inorganic Analysis

Solid Carbon Dioxide [and Liquefied Fermentation Gas]. A. J. C. Cosbie. (*J. Inst. Brewing*, 1932, **38**, 427–439.)—Solid carbon dioxide ("dry ice") is now produced in this country on a commercial scale, being transported in suitably insulated containers, and with only a small loss due to evaporation. An account is given of the author's method of utilising the solid product as a motive force for moving beer from place to place in a bottling department, and as a substitute for "tube" gas for carbonating beer. Solid carbon dioxide has about three times the refrigerating capacity of water ice. The inert constituents (about 0·2 per cent.) in "tube" gas are chiefly hydrogen and nitrogen, whilst in solid gas they are oxygen and nitrogen. The commercial gas from six cylinders did not, in any instance, exceed a purity of 98·5 per cent. of carbon dioxide immediately the cylinder was opened, whilst with the liquefied product from the solidified gas the first sample drawn contained 99·80 per cent. of carbon dioxide. The "tube" gas derived from a brewery differs from that obtained from solid carbon dioxide in containing a large proportion of impurities. Analysis of the drainings from fermentation "tube" gas gave the following results: Sp.gr., 0·895; acidity (as acetic acid), 0·36 per cent.; nitrogen, 0·05 per cent. By fractional distillation the liquid was separated into five fractions ranging from 171·5° F. to 213·1° F., leaving 4 per cent. of an "oily layer," and 3·5 per cent. of sludge. The main fractions consisted largely of ethyl alcohol, with small quantities of aldehydes, ketones and esters, and traces of iso-propyl alcohol. These substances are presumably responsible for the odour of "tube" gas.

Simple Method for the Determination of Argon. H. Copaux. (*Bull. Soc. Chim.*, 1932, **51**, 989–992.)—In the following method for the determination of argon in air and industrial gases, heated lithium metal is used for absorbing the nitrogen, etc. The gas is introduced into a Pyrex tube, 40 cm. × 15 cm. in diameter, of wall thickness not less than 2 mm., drawn out at one end and fitted with a sealed-on manometer at the other end, and containing two boats holding, respectively, phosphorus pentoxide and 0·25 grm. of lithium metal. The tube is sealed and the pressure of the confined gas is noted. The tube is heated to bring the lithium to a dull-red heat, until the internal pressure remains constant. The proportion of argon (together with other inert gases, which are usually in insignificant amount) is given by the ratio of the residual and initial pressures. If the gas contains notable proportions of oxygen or hydrogen, a third boat containing reduced copper or copper oxide, respectively, should be placed in the tube. The presence of hydrocarbons in the gas analysed introduces difficulties, unless further refinements, which it was desired to avoid in this simple method, are adopted.

S. G. C.

Determination of Lead and other Metals in Iron Salts. A. D. Powell and G. F. Hall. (*Pharm. J.*, 1932, **129**, 247.)—The iron salt, containing from 0·5 to 1 grm. of iron, is dissolved in 20 c.c. of hydrochloric acid (25 to 27 per cent. w/v), and strong nitric acid is added in sufficient quantity to oxidise any ferrous iron (0·5 to 2·5 c.c.). The solution is boiled, cooled, and, if prolonged oxidation is necessary, the hydrochloric acid concentration is adjusted. The cold solution is treated in an extractor with three 20-c.c. portions of ether, and a fourth extraction is made if the acid solution is still coloured. The acid solution is heated in a narrow-necked flask on a steam-bath until the ether has volatilised, the acidity is almost neutralised with ammonia, potassium cyanide is added, and the lead test is completed by the usual Pharmacopoeial method. Any zinc, copper, nickel, or manganese remain in the acid solution after the extraction with ether. A series of determinations on 19 samples of iron ammonium citrate from various sources showed that the lead varied from 25 to 600 parts per million, but 50 parts is regarded as a reasonable limit. D. G. H.

Volumetric Determination of Mercuric Chloride by Rupp's Method. H. Brindle. (*Pharm. J.*, 1932, **129**, 245.)—The chief drawback of the Rupp method for determining mercuric chloride is the difficulty of dissolving the precipitated mercury in the iodine solution, and this was overcome by shaking for one minute with 5 ml. of a mixture of 2 vols. of B.P. ether and 1 vol. of B.P. chloroform before titrating the excess of iodine. D. G. H.

Determination of Traces of Mercury in the Form of Rings of Mercuric Iodide. A. Delauney. (*Ann. Falsificat.*, 1932, **25**, 409–412.)—The metal on which mercury has been deposited electrolytically is heated in a horizontal tube in a current of air, the mercury being condensed on a cool part of the tube and afterwards subjected to the action of hot air containing iodine vapour. The mercuric iodide thus formed is driven forward and collects on the walls of the tube as a ring, which is compared with standard rings prepared similarly. The portion of tube with the ring may be sealed off if required. As little as 0·01 mgrm. of mercury is thus detectable. Full details of the procedure are given.

T. H. P.

Detection of Small Quantities of Bismuth with *o*-Hydroxyquinoline. R. Sazerac and J. Pouzergues. (*Compt. rend. Soc. Biol.*, 1932, **109**, 79–82; *Ann. Chim. Anal.*, 1932, **14**, 406.)—*o*-Hydroxyquinoline, used in conjunction with potassium iodide, gives a double-iodide reaction with bismuth, which is claimed to be more characteristic than that given by the more commonly used cinchonine or quinine. With a solution containing less than 1 part per 100,000 of bismuth a flocculent, orange-red precipitate is produced; the precipitate appears under the microscope as clusters of orange-red prismatic crystals; with stronger solutions of bismuth the precipitate is partly amorphous, unless formed in presence of about 1 per cent. of nitric acid in the liquid. Iron does not interfere. The reagent is a 2 per cent. aqueous solution of *o*-hydroxyquinoline which is mixed with an equal volume of 4 per cent. potassium iodide solution immediately before use.

S. G. C.

Determination of Mercury, Zinc, Fluorine and Arsenic in Impregnated Wood. Anon. (*Chem.-Ztg.*, 1932, **56**, 730–731.)—The following methods have been tested for the analysis of wood impregnated with preservatives as under. The samples of wood used should be cut into pieces about the size of matches. *Mercury compounds* (usually mercuric chloride).—To 100 grms. of the wood are added 500 c.c. of dilute hydrochloric acid (12·5 per cent.) and 40 c.c. of sodium chlorate solution (20 per cent.). The liquid is boiled under reflux for 1 hour and filtered. This extraction process is repeated twice with weaker acid (2·5 per cent.), and with 20 c.c. of the sodium chlorate solution. The combined extracts, after the addition of 50 c.c. of the sodium chlorate solution, are boiled under reflux until evolution of chlorine ceases, after which the hot solution is transferred to a beaker, and some kieselguhr and 10 c.c. of stannous chloride solution (10 per cent.) are added, with stirring. After 10 minutes the precipitate is filtered off on a Gooch crucible with an asbestos mat. The mercury in the precipitate is dissolved from the crucible by heating it in a beaker with 30 c.c. of concentrated sulphuric acid, and the diluted solution is titrated in the usual manner with 0·1 *N* ammonium thiocyanate solution, with 2 c.c. of a saturated nitric acid solution of iron alum as indicator. *Zinc compounds* (usually zinc chloride).—A sample of the wood is heated at the lowest possible temperature until completely carbonised; ashing is unnecessary. An excess of dilute hydrochloric acid is added to the residue, and the liquid is heated to boiling, then neutralised, made strongly ammoniacal and filtered, the zinc-content being determined in the usual manner. *Fluorine compounds.*—A 10- to 100-grm. sample is saturated with a calcium acetate solution [prepared by dissolving 30 grms. of calcium carbonate in 300 c.c. of dilute acetic acid (25 per cent.), and diluting the solution to 1 litre], and ashed. The ash is wetted with dilute acetic acid (25 per cent.), plus a few drops of 10 per cent. potassium iodide solution (the purpose of the latter being to reduce any manganic oxide), and the whole is evaporated to dryness on a water-bath. The residue is extracted with water, then filtered off and washed, and ultimately ignited. The fluorine in the residue is determined by evolution as silicon tetrafluoride according to Penfield's method, as described in Treadwell's *Analytical Chemistry*, Vol. II.

Arsenic compounds.—To 20 to 50 grms. of the wood, contained in a wide-necked 1-litre flask, are added 6 grms. of barium chloride, 10 grms. of ferrous sulphate, and sufficient concentrated hydrochloric acid to cover the wood. The flask is closed by a stopper carrying the following attachments: (*a*) Tap-funnel, (*b*) leading tube, (*c*) splash-bulb attached to a Liebig's condenser. The liquid is distilled in a slow current of air until evolution of hydrochloric acid gas ceases and the liquid boils quietly, the exit end of the condenser dipping below the surface of 300 c.c. of water; a further 100 c.c. of hydrochloric acid are added to the flask and the distillation is continued. The arsenic in the distillate is titrated with iodine, after neutralisation, in the ordinary manner. [The paper is a communication from the Laboratory for Wood Preservation of the Rütgers Co., Berlin.]

S. G. C.

Electrolytic Determination of Gallium: Prevention of Anodic Platinum Losses. E. Reichel. (*Z. anal. Chem.*, 1932, 89, 411–421.)—In the electrolytic determination of gallium (ANALYST, 1932, 334) the anodic solubility of platinum is appreciable. It was found that hydrazine and hydroxylamine act as efficient depolarisers while not interfering with the determination. Correct results were obtained with an electrolyte consisting of water, 100 c.c.; strong ammonia, 25 to 35 c.c.; ammonium sulphate, 20 grms.; and hydrazine sulphate, 6 grms.; and with 1400 R.P.M., 1·7 volt, 5 amp., temperature 70° C., duration

30 minutes. With quantities of gallium exceeding 0·1 grm., the duration and the amount of hydrazine salt added were increased. The addition of hydrazine or hydroxylamine sulphate was likewise beneficial in the case of ammoniacal zinc, nickel, and cobalt solutions submitted to electrolysis. W. R. S.

Determination of Cobalt by Means of Nitrosonaphthol. C. Mayr and F. Feigl. (*Z. anal. Chem.*, 1932, 90, 15–19.)—The precipitation of cobalt by α-nitroso-β-naphthol involves oxidation to the cobaltic state at the expense of the reagent, the reduction products being partly co-precipitated; hence the precipitate is not of stoichiometrically constant composition, and must be ignited to oxide. A pure precipitate, which can be used for gravimetric determination after drying, can be obtained as follows: The cold, weakly-acid chloride, sulphate, or nitrate solution (10 to 20 c.c.) is treated with 5 to 10 drops of hydrogen peroxide (perhydrol) and a slight excess of 2 *N* sodium hydroxide solution, then with 10 to 20 c.c. of glacial acetic acid; the precipitate is dissolved by warming, if necessary. The volume is made up to 200 c.c. with boiling water, and 10 to 20 c.c. of the reagent (a 2 per cent. solution of nitroso-β-naphthol in 50 per cent. acetic acid) are added. The liquid is vigorously stirred and boiled, the precipitate coagulating. After settling, it leaves the supernatant liquid clear and yellow. The precipitate is collected in a tared porous porcelain crucible, and the beaker is cleaned with 3 portions of hot acetic acid (1:3 water). The precipitate is finally washed four times with boiling-hot water, and dried at 130° C. until constant in weight. Factor Co: $[C_{10}H_6O(NO)]_3Co.2H_2O = 0{\cdot}0965$. Precipitates containing more than 0·25 grm. of metal are bulky and require several hours' drying. The procedure separates cobalt from nickel, zinc, and aluminium, provided the precipitation is carried out at a higher acidity (up to 50 per cent. acetic acid for high nickel ratios); it provides a better separation from nickel and aluminium than electrolysis.

W. R. S.

Determination of Rhenium. E. Kronmann. (*Z. anal. Chem.*, 1932, 90, 31–34.)—The stepwise concentration of rhenium by fractionation, for which several methods have been proposed, is tedious and rather uncertain. Some rhenium may be lost by volatilisation in the acid attack, while a small amount may remain with the insoluble residue in the subsequent filtration. The author submits the mineral to acid attack combined with distillation in a large all-glass apparatus (illustrated by two diagrams). The powdered mineral (250 to 1000 grms.) is treated with nitric acid, the nitrous fumes passing a cooler and escaping through a specially constructed receiver. The distillation is carried out in a current of air or hydrogen chloride, and the rhenium in the distillate is determined with nitron acetate. The procedure is not given, but reference is made to the papers describing it. W. R. S.

Selenium as a Catalyst in the Kjeldahl Method for the Determination of Nitrogen in Coal and Coke. H. E. Crossley. (*J. Soc. Chem. Ind.*, 1932, 51, 237–238T.)—The advantages of selenium over mercury as a catalyst in the determination of nitrogen by the Kjeldahl process in flour, etc., found by Lauro (ANALYST, 1931, 56, 813) have now been found to apply also to coal and coke. With the sulphuric acid mixture, as recommended in the Fuel Research Board method (*Dept. Sci. Ind. Research, Physical and Chemical Survey of National Coal Resources*, Report No. 7), the time taken for a clear liquid to be produced in the digestion of a coal sample was 40 minutes with the selenium catalyst and 87 minutes with the mercury catalyst. The time required for coke was 30 minutes less with selenium than with mercury. S. G. C.

Microchemical

Micro-Determination of Carbon and Hydrogen in an Atmosphere of Nitrogen. J. B. Niederl and B. Whitman. (*Mikrochem.*, 1932, 11, 274–300.)—The chief source of error in the Pregl method of micro-combustion is the use of lead peroxide, which absorbs the oxides of nitrogen and sometimes some carbon dioxide. and water also. When the combustion is carried out in an atmosphere of nitrogen, lead peroxide is dispensed with, the apparatus is simplified, and the time of combustion and sweeping-out of the tubes is reduced from 44 to 22 minutes. The filling of the tube consists of a length of 15 mm. of silver wire or wool, then 70 mm. of fine wire-form copper oxide, a wad of asbestos, 30 mm. of a mixture of equal parts of lead chromate and wire-form copper oxide, another plug of asbestos, and then 60 mm. of wire-form copper oxide, followed by a small plug of silver wire, then 30 mm. of reduced copper, another silver plug, and, finally, 115 mm. of wire-form copper oxide. The apparatus is the same as that used for the Pregl method, except that, as only nitrogen is used, only one gas-holder and pressure-regulator is necessary. The constant-temperature bath may be replaced by a cylinder of copper surrounding the tube, which is heated at one end by the long burner. This maintains the end of the tube at a sufficiently high temperature to prevent the condensation of moisture before reaching the absorption tubes. The combustion, which is carried out at a rate of flow of nitrogen of 5 c.c. per minute, takes 15 minutes, and a further 5 minutes is sufficient to sweep out all the products of combustion. The absorption tubes are then removed from the combustion tube, and 50 c.c. of dry air free from carbon dioxide are drawn through, a Marriotte flask being used, so as to replace the nitrogen by air; this takes only 2 minutes. The tubes are then wiped and weighed. The method of introducing the sample is to be further improved: for volatile or subliming substances about 4 cm. of powdered copper oxide powder are placed in the charged combustion tube, and the substance is introduced into a platinum boat placed close to the copper oxide. Substances of unknown composition and those hard to burn should be mixed with the powder-form copper oxide in the tube. The sample is weighed out into a small platinum scoop, which is dropped into the combustion tube in a vertical position, the scoop is removed with a wire loop, and the sample is mixed with copper oxide with a piece of platinum wire. Liquid samples are weighed out as in the Pregl method. Good results are obtained, and the method is simpler than the Pregl method for those unskilled in micro-combustion.

J. W. B.

Determination of the Volatile Constituents of Copper-Zinc Alloys. L. I. Weinstein and A. A. Benedetti-Pichler. (*Mikrochem.*, 1932, 11, 301–310.)—The sum of the volatile constituents of copper-zinc alloys can be rapidly determined on samples of a few mgrms. in weight by heating them at 1150° C. for 10 minutes in a gentle current of hydrogen. The hydrogen, which is generated in a Kipp apparatus and washed in dilute sodium hydroxide solution, passes through 1 metre of thin-walled rubber tubing (3 mm. bore) to the quartz combustion tube at the rate of 2 bubbles per second. The tube is heated electrically; it is 35 cm. long and of 8 mm. bore, and is tapered to a capillary of 0·5 to 1 mm. bore and 10 mm. long. The substance is weighed into a porcelain boat and is heated in the heating tube for 15 minutes. Simple alloys of copper and zinc gave good results. Commercial alloys containing a number of constituents gave a loss of weight slightly higher (1 or 2 per cent.) than that calculated for the total weight of volatile constituents. J. W. B.

New Microchemical Test for Molybdenum, Vanadium and Tungsten. A. Martini. (*Mikrochem.*, 1932, **12**, 112–113.)—*Molybdenum.*—A drop of a 1 per cent. solution of ammonium molybdate solution is placed on a slide, a little powdered pyrocatechol is added until the solution is orange-red, a drop of benzylamine is added, followed by a drop of aqueous acetic acid (1:5), and the mixture is stirred with a glass rod. Orange streaks appear, which under the microscope are seen as sheaf-shaped crystals. *Vanadium and Tungsten.*—The test is carried out in the same way, 1 per cent. solutions of salts of the metals being used. Vanadium forms pale yellow crystals, tungsten black crystals in the form of rosettes. The reactions take place in even more diluted solutions. Photomicrographs of the crystals are given. J. W. B.

Reviews

MICROCHEMICAL LABORATORY MANUAL. By FRIEDRICH EMICH. With a section on SPOT ANALYSIS, by DR. FRITZ FEIGL, translated by FRANK SCHNEIDER. Pp. xvi+180 with 83 illustrations. London: Chapman & Hall. 1932. Price

This is a translation of the "Mikrochemisches Praktikum," 2nd edition, already reviewed in this journal (ANALYST, 1931, **56**, 138). It is the only textbook describing in detail both qualitative and quantitative inorganic micro methods, and an English translation was badly needed. The translation has been very carefully and efficiently carried out by Mr. Schneider, and if, at times, the German construction of the sentence has been retained in the translation, the meaning is always clear.

The translator retains the German word "schlieren" in his description of the phenomenon which might have been called "liquid striation" (as in *Recent Advances in Analytical Chemistry*, Vol. II, *Microchemistry*), and this is clearer for readers not familiar with German. Since Professor Emich's companion book, the *Lehrbuch*, has not also been translated, it is a pity that the very useful table of inorganic qualitative tests in that book could not have been included in the English edition of the Laboratory Manual. The Manual is, however, a most valuable and comprehensive book, covering the whole of inorganic microchemistry, including "spot" tests, on which there is a very brief article by Dr. Feigl, the leading authority on the subject.

JANET W. BROWN

WATER ANALYSIS FOR SANITARY AND TECHNICAL PURPOSES. By HERBERT B. STOCKS. Second Edition, revised and enlarged by W. GORDON CAREY, F.I.C. Charles Griffin & Co. 1932. Price 7s. 6d.

This little book was originally (1912) written "For the use of Public Analysts, Medical Officers of Health, and Students who are interested in this branch of Analytical Work." The new edition is very largely a reprint of the first, the main differences being the omission of the description of Frankland and Armstrong's method for the determination of organic carbon and nitrogen, and the addition of paragraphs on the determination of hydrogen-ion concentration, of free chlorine, and of iodides, and a short section on the bacteriological examination of waters. The chemical section of the book runs to 93 pages, the bacteriological section to 10, and eight appendices are contained in 28 pages more. These appendices are respectively: (1) Standards of Purity Recommended by the Rivers Pollution Commission, (2) Standards of Various Authorities for Effluents, (3) Average Composition of Unpolluted Water, (4) Tension of Aqueous Vapour, (5) Reduction of Cubic Centimetres of Nitrogen to Grams, (6) Table for Converting c.cs. of Indigo Solution to Parts of Nitrogen per 100,000, (7) Preparation of Reagents needed for Water Analysis, (8) Preparation of Culture Media for Bacteriological Examination of Water. An index of 5 pages completes the book.

As a text-book for beginners the book will serve its purpose very well; the methods of analysis are described carefully and in sufficient detail, and the inferences to be drawn from the results of analysis are justly and moderately stated. But it is to be regretted that a more thorough revision was not undertaken, and that the reviser has been so tender towards the original content and phraseology, for considerable improvement might have been made, without adding to the bulk of the volume. Burgess' method of comparing the colours of waters is mentioned, but it is not described, nor is a reference to Burgess' paper given; the use of aluminium foil or Devarda's metal instead of the copper-zinc couple in determining nitrates by reduction to ammonia might well have been mentioned, as might also Houston's methods of comparing the lead-solvent and erosive powers of waters. Space for these and for one or two other desirable additions might easily have been found by the omission of the four illustrations, which convey nothing that could not be understood from the descriptions, and in the last of which a bulb described in the letterpress as "pear-shaped" is shown as a very perfect sphere.

A more drastic revision would have allowed the reviser in many places to improve the language in point of accuracy or clearness; the expositions of the method of calculating results are frequently anything but clear—on p. 29, for instance, the word "amount" is used in two successive lines, and means "volume" the first time and "weight" the second, and on the same page the expression "Log of 1 c.c. N_2" occurs, as though there could be a logarithm of anything but a numerical quantity.

Our old friends "estimate" and "determine" hobnob with great friendliness throughout the book; on p. 5 we "estimate the amount and determine the proportion"; on p. 47 "the estimation of hardness comprises the determination of two factors"; and so on. Again, the author is one of those, all too numerous now among the writers of scientific and technical papers and books, who worship "the latter"—on p. 4 we wash with water until "the latter" is neutral; on p. 18 a method for determining organic matter yields figures having no relation to the amount of "the latter"; and on p. 26 we have "of the former," where "indigo" would be not only more forcible and clear, but shorter. The book is full, too, of singular subjects with plural verbs or the converse, and we have on p. 10 a pipette requisitioned which shall be "easily" emptied—what is meant is "quickly," for the "ease" of emptying has nothing to do with the time. These may seem small things, but they irritate, and the writer of a scientific text-book should be scrupulous about them. He is inculcating accuracy (or ought to be), and his language should illustrate it. It is a pity that the opportunity given by revision for improvement in this respect should not have been seized.

Of purely typographical errors there are few—a transposition of letters in "formation" on p. 14, and the omission of N from 1/3200 N on p. 116 are all I have noticed. But a much more important error, possibly typographical, occurs twice on p. 41, in the omission of the brackets that should surround (38—12).

The directions for bacteriological examination are very concise and clear, and perhaps increase one's regret that Mr. Carey has not written a fresh text-book on water analysis instead of being under the restrictions necessarily involved to a greater or less extent in revision—though one may perhaps ask whether the language of the football field has yet crystallised into standard English so far as to permit one to speak of negotiating a reservoir.

Taken with all its minor faults, it is a useful little book, though a better one, of similar size and scope, is much to be desired. J. T. DUNN

THE PREPARATION OF PURE INORGANIC SUBSTANCES. By E. H. ARCHIBALD. Pp. 383. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1932. Price 23s.

In producing this volume, Professor Archibald, who occupies the chair of Analytical Chemistry at the University of British Columbia, has earned the thanks of all research workers to whom pure chemicals are an absolute necessity, and who themselves have to carry out methods of purification in order to obtain material in as near a state of absolute purity as possible. The book consists of a collection of the methods for preparing pure chemicals employed by the leading scientific research workers during the past thirty years. In the preface the author states that what are thought to be the most dependable and simple of these methods are set forth, and that only those methods of procedure have been included which have been proved to produce what we may consider pure substances.

In Chapter I, purification processes in general, and the most suitable materials for the necessary apparatus, are discussed. Centrifugal draining and washing are recommended as the most efficient way of removing the mother liquor from crystals, and Richards' work on these lines is quoted. In the subsequent chapters, the whole of the elements, with the exception of the following, are dealt with: Ma, Rh, Nd, Il, Eu, Gd, Tb, Yb, Lu, Hf, Re, Os, Ir, Po, Nt, Ac, and Pa. The chapters are arranged systematically, according to the periodic table, and Chapter II deals with the zero group, helium, neon, krypton, and xenon; Chapter III, with group IA, comprising hydrogen, lithium, sodium, potassium, rubidium and caesium, and so on.

Methods for the preparation of the pure element are described in some cases, of one or more of the pure salts in other cases, or of both element and salts. Copious references to the original papers are given and twenty line drawings of special apparatus are figured; the book is well indexed, there being a subject index and an author's index occupying 13 pages.

This is a very readable book, and will be a useful addition to the shelves of all scientific libraries. The author's style is very lucid, explanations of the various stages of the methods are given in simple language, and, apart from the spelling of sulfur, sulfate, and cesium, the text is free from Americanisms.

T. TUSTING COCKING

ANTIQUES; THEIR RESTORATION AND PRESERVATION. By A. LUCAS, O.B.E., F.I.C. Second Edition. Pp. 240. London: Edward Arnold & Co. 1932. Price 8s. 6d. net.

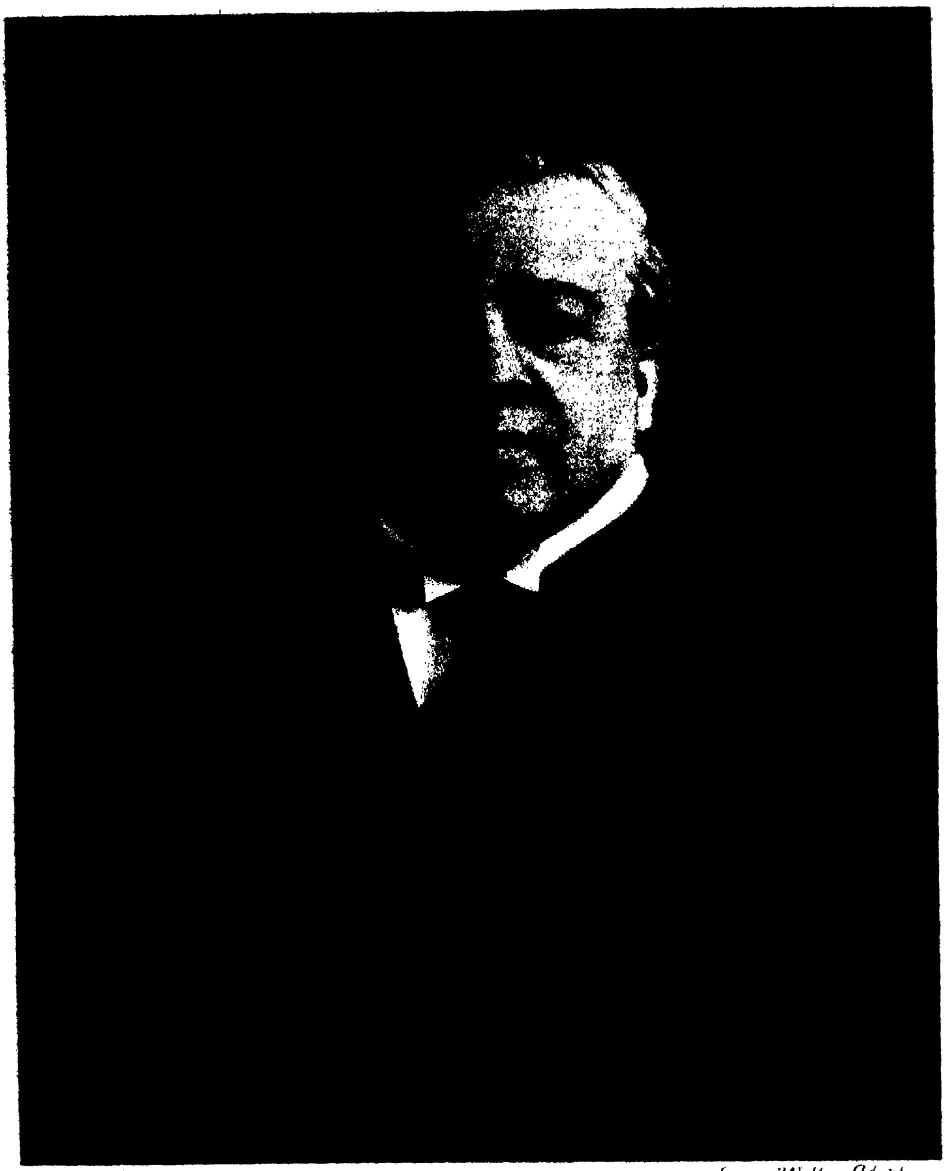
In the new edition of his practical little handbook Mr. Lucas rightly lays stress upon the importance of chemical knowledge for the successful cleaning or restoration of museum objects. This is now widely recognised, and the directors of the most important museums either have a chemist on their staff or constantly consult one. The curators of small museums, however, can seldom avail themselves of expert assistance, and for all such this book will prove invaluable, not only by giving directions how to treat the various objects, but also by showing what methods should be avoided. As the author points out, some positively injurious methods continue to be recommended, owing to the fact that for the time being they appear to have been successful, and nothing is said about the condition of the objects after the lapse of a year or two.

The new edition follows the general arrangement adopted in its predecessor (*cf.* ANALYST, 1925, **50**, 102), the first two chapters dealing with the general methods of cleaning and preservation, and the third with the application of those methods to objects of specific materials, including metals, plaster, wood and stone. The section on pictures is very complete, and the treatment most suitable for each class (oil paintings, water colours, tempera, etc.) is described in detail. Finally, there is a chapter on simple physical and chemical tests, which will help curators without chemical knowledge to identify the material of which a specimen is composed, and the book concludes with a useful bibliography and a good index.

During the last eight years the author has had almost unrivalled opportunities of studying this subject practically in connection with the preservation of the objects found in the tomb of Tut-ankh-amūn, and of specimens in the Cairo museum, and he embodies the results of his experience in this book, which contains so much new matter that the 135 pages of the first edition have now become 240.

Although, as has been mentioned, the book is primarily intended for those with little, if any, scientific knowledge, it will also be of great use to all chemists who are likely to be consulted on the preservation of structural materials.

EDITOR



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DECEMBER, 1932 Vol. LVII., No. 681

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, November 2nd, the President, Mr. F. W. F. Arnaud, being in the chair.

Certificates were read in favour of:—Ernest Edward Unwin Abraham, B.Sc., F.I.C., Enid A. M. Bradford, B.Sc., Frank Brookhouse, B.Sc., A.I.C., Gerald Harry Edwards, B.Sc., A.I.C., Jack Firth, A.I.C., Albert E. Fletcher, F.I.C., Patrick Sarsfield MacMahon, M.Sc., F.I.C., Moses Puffeles, Edgar Alexander Raynor, B.Sc., A.I.C., Bernard Joseph Styles, Viscount Tiverton, Cecil Edgar Wiseman, B.Sc., A.C.G.F.C.

The following were elected Members of the Society:—Lionel James Dent, B.Sc., Leonard Arthur Haddock, B.Sc., A.I.C., Arthur Littlewood, M.A., A.I.C., and John Henry Weber, B.Sc., A.I.C.

The following papers were read and discussed:—"Observations on Changes in Raspberries after Picking," by Theodore Rendle; "The Separation of Uranium from Tantalum, Niobium and Titanium," by W. R. Schoeller, Ph.D., and A. W. Webb (*Work done under the Society's Analytical Investigation Scheme*); "A New Form of Filter Stick: Its Use in Gravimetric Analysis," by A. J. King (demonstrated by Janet W. Brown, Ph.D., A.I.C.); and "A New Method for the Iodimetric Titration of Phenols," by F. J. Warth.

Obituary

ALFRED CHASTON CHAPMAN

By the death of Alfred Chaston Chapman, on October 17th, 1932, a notable and greatly-esteemed figure in the chemical world has passed from our midst.

His attainments in the realm of chemical science, and more particularly in the domains of analytical chemistry and the brewing industry, mark him out as one of the most brilliant workers we have had during the last 40 years, and, as a pioneer in analytical chemistry within this period, he can rightly be classed with such "giants" as Alfred H. Allen and Otto Hehner.

In addition, however, to his achievements in these spheres, Chapman did what few other professional men of his time succeeded in doing, as he was able to convince the theoretical and purely scientific worker that analytical chemistry, while it might be followed as a profession, had yet a place as a true science and could contribute materially to the advancement of chemical knowledge. Chapman, indeed, by his example, helped to raise the profession of analytical chemistry to a position where it commanded recognition from the whole chemical and scientific world. Hitherto it had been too much the habit to regard the analytical chemist as one who pursued his practice, not with the idea of advancing science, but mainly for his own emolument. Chapman, by his work in various branches, not merely gained the professional success which his labour merited, but pursued his work in a genuine scientific spirit, having before him the attainment of truth and the advancement of his science.

Such an achievement has succeeded in putting the entire branch of analytical chemistry on a different footing from that which it occupied at the time he began his work, and Chapman has laid the whole class of professional chemists under a deep obligation to him for the unique services that he rendered.

The Society of Public Analysts, in particular, has reason to be profoundly thankful to him for what he did in their interests, and the present tribute to his memory is written by one who was his contemporary during all his working period, but who feels himself able to speak but inadequately of the influence for good which Chapman exercised and of the way in which, by his conduct and example, he succeeded in raising to its right position the profession to which they equally belonged.

But, besides the prosecution of his own practice to such useful ends as were accomplished, Chapman did a great deal more, in that he set a high standard of professional conduct and further devoted his energies and means to the advancement of the interests of his professional brethren. This he was enabled to do, not merely through his eminence in his particular branch of science, but by his personal character, his high sense of honour, and those qualities of kindliness, consideration, and sound judgment which endeared him to all who knew him, besides making him, in numerous spheres, an able and valued public servant.

Chapman was essentially a strong man, one who could speak and act forcibly, whose utterances, delivered clearly and concisely, carried conviction with them by their evident honesty of purpose, and it is no wonder that he was early selected to be Chairman of many scientific, professional, and industrial associations, and rendered valuable help in Government and other public enquiries.

The closing ceremony of October 20th was a fitting tribute to the esteem and affection in which Chapman was held by his scientific and professional brethren, who gathered there in representative capacity on behalf of the various organisations with which he had been connected, as also in their personal capacity. The Society of Public Analysts and Other Analytical Chemists naturally was well represented.

Since the journals and periodicals of other Societies have dealt with Chapman's life and work more particularly as regards his connection with them, it is fitting that the present record should be concerned mainly with his work in the analytical field, and his association with the Society of Public Analysts. Of the latter he became a member in 1895, served on the Council in 1897–8, was secretary in 1899, and continued to hold this office until his elevation, in 1914, to the Presidency, which position he occupied for the usual biennial period.

Born in 1869, Chapman received his early education at Leeds Grammar School; then, on the family coming to London, he began his chemical training at University College, London, his teachers being Professors Alexander Williamson and Charles Graham, with the latter of whom he was subsequently closely associated. At University College he became demonstrator in chemical technology, and, after a short period as assistant to Graham, he took the step of setting up for himself in practice as an analytical and consulting chemist. None but a man of determined energy would in those days have ventured on such a course, but this, Chapman—with a truly scientific aim before him and the will to succeed, aided, no doubt, by the possession of a financial competency—essayed to do, and began work in Leadenhall Street, primarily in relation to the brewing industry. It was not long before he established a practice for himself, and soon had to move to larger premises in Duke Street, Aldgate, where he remained until the close.

He not only built up a successful practice, at first chiefly connected with the brewing industry, but he was soon surrounded by a number of pupils, who found in him a ready and able teacher, and, under his guidance, frequently passed to positions of responsibility. Not only was Chapman thorough in his teaching, but he was imbued with the true spirit of scientific enquiry, so that, whilst he came to be an authority in the brewing world, his independent research work, which mainly occupied his interest, found its outlet in many different fields. Hence we find him working at the problems of fermentation generally, and his contributions to the literature of that division of chemistry are of the highest value. In particular, his researches on the essential oil of hops and its antiseptic significance excited much attention, while in later years the problems of bio-chemistry engaged his interest closely.

Very shortly after starting practice on his own account as an analytical and consulting chemist, Chapman began the series of contributions to technical, analytical and chemical journals which continued to the end of his career. His earliest writings were on matters connected with brewing, and were contributed (from 1893 on) to the *Journal of the Institute of Brewing*. Of these, the most important, perhaps, were those on the "Essential Oil of Hops" (1895, 1898, 1903, and 1929). His work on the preservative properties of hops is well known; he elaborated biological methods for the determination of the preservative value of hops and also methods for the determination of tannin (1907–9). The Standardisation of Analytical Methods in relation to the analysis of brewing materials formed the subject of other papers sent to the *Journal of the Institute of Brewing*.

Chapman commenced his written contributions to THE ANALYST in 1899 with a paper on the quantitative separation of isovaleric and acetic acids. This was followed, in 1900, by one putting forward a method for distinguishing hops and quassia. The same year (1900) came the notable arsenic "scare," which led to the appointment, in 1900, of a Royal Commission on Arsenical Poisoning in Food, before which Chapman gave evidence. In the report of the Royal Commission (1902) a general maximum for the proportion of arsenic in food was laid down, and it was shown that the Marsh–Berzelius test, as modified by Chapman and others, was capable of detecting far less than this proportion.

In this connection Chapman did much valuable work which greatly assisted the Royal Commission, and he contributed to THE ANALYST a number of papers on the methods of determining arsenic (1901, 1904, 1906, and 1907), these culminating in 1907 with his discovery that the coating with cadmium of the zinc used in the Marsh–Berzelius method for determination of arsenic, removed the difficulties that had been so frequently experienced with regard to the "insensitiveness" of the zinc.

While it is for his contributions to the subject of the determination of arsenic and the methods that he devised in that connection that analytical chemists will mainly remember his work, his researches covered a far wider field in the domain of analytical chemistry.

Thus, we find him dealing extensively with essential and other oils from various sources. Already, in 1900, he had sent to THE ANALYST a communication on an improved absorption apparatus for use in the analysis of essential oils, followed, in 1907, by a note on camphorated oil, and a paper in 1912 on the examination of Chinese and Japanese wood oils. Later he turned to the examination of fish oils, and papers on the occurrence of hydrocarbons in fish-liver oil, on dog-fish liver oil, and on liver-oil of the tope, appeared in THE ANALYST in 1917, 1918, and 1922, respectively.

Nor must his communications to the *Journal of the Chemical Society* on spinacene and its derivatives (1917, 1918, and 1923) be forgotten. In these, mention is made of the curious hydrocarbon which he had found to constitute nearly 90 per cent. of the oil yielded by the livers of certain shark-like Mediterranean fish.

His work on the essential oil of hops, in particular, was of a high order, and contributed largely to our knowledge of their action and value. Papers on this subject and on fermentation in general naturally found a place primarily in the *Journal of the Institute of Brewing*, but several on this and allied subjects occur also in the *Journal of the Chemical Society* (1895, 1903, 1914, 1928, and 1929).

Yet other subjects on which Chapman wrote in THE ANALYST were Methods for the Estimation of Tartaric Acid (1907) and of Creatinine (1909), Malt Vinegar Standards (1912), Detection and Separation of Dye-Stuffs (1912), and (1926) the presence of arsenic and of lead and other metallic impurities in crustaceans and shellfish.

Chapman took a great interest in the advance of bio-chemistry as a separate branch of science, and, in addition to his earlier work on fermentation, he contributed papers on the nature and action of yeast, and on certain species of fungi. He was, indeed, the first (1926) to advocate the establishment of an Institute of Industrial Micro-biology, a hope that has not, as yet, materialised.

This by no means exhausts the list of Chapman's contributions, but will serve to indicate the great activity he displayed and his desire to add to chemical knowledge in practical directions.

Just as Chapman's tenure of the Secretaryship of the Society of Public Analysts was marked by much activity and a decided advance of the Society, so, too, his occupancy of the Presidential chair during the years 1914 and 1915 is memorable on two special accounts—the first, his Presidential addresses at the close of each session; and the second, the impetus given to the Analytical Investigation Scheme of the Society, which has materially assisted in the accomplishment of much good work by members of the Society, and has greatly enhanced the value of the pages of THE ANALYST.

This scheme was originally suggested by Chapman in 1904, when he was Secretary, and it met then with a fair success, papers embodying work carried out under it being, from time to time, contributed to THE ANALYST. But it was when Chapman became President that the scheme was more actively worked, and the co-operation of university professors and teachers was enlisted in its support. It can, indeed, now be regarded as an integral part of the Society's operations.

Chapman, while still Secretary, had represented the Society at the International Conference on the Unification of Methods of Food Analysis, held in Paris in 1910, and, not long after coming into office as President, found himself faced by the many difficult problems arising out of the war. In these, so far as his own science was concerned, he notably bore his part, concerning himself in particular with such matters as the supply of apparatus and reagents of British make.

In 1914 also, during his Presidency, the first joint meeting with the newly-formed Biochemical Society was held.

The addresses which Chapman gave at the close of each session of his tenure of the Presidency were masterpieces of their kind, and, in his insistence on the recognition of analytical chemistry as a branch of science and as calling for the establishment of Chairs of Analytical Chemistry in Universities and Colleges, he rendered lasting service to the cause he had at heart. But, perhaps, even more than this, his addresses—and more particularly that given on his relinquishing his office of President in 1916—constituted most able and powerful expositions of the work that analytical practice had been able to accomplish in late years, and of the position which it should occupy in the future.

It is not surprising, albeit a source of much satisfaction to all who had known him and his work, that this was followed by his election to the Fellowship of the Royal Society in 1920, largely as a result of his contributions to analytical chemistry.

To detail the many offices that he held and the various Enquiries and Commissions on which he served, would be but to repeat what has been already set out elsewhere. To the professional chemist it will suffice to record his services as Examiner, and later (1921–4) as President of the Institute of Chemistry, and the ever-ready support which he gave to all professional objects that called for his help.

Chapman's personality was a lovable one, and, backed up, as he was, by his able and energetic wife, and aided by his own high sense of honour and his sound judgment, he was privileged to confer, in the comparatively short period of his life, great and lasting benefits on the profession of which he was so eminent and esteemed a representative.

J. A. VOELCKER

Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates

XXIV. An Improved Method for the Separation of Tantalum from Niobium

By W. R. SCHOELLER, Ph.D.

(Work done under the Society's Analytical Investigation Scheme)

This Section furnishes another instance of the progressive refinement we have been able to introduce in our methods as the result of continued study and practical application. In Section IV (Analyst, 1925, **50**, 485), Powell and Schoeller described a new method for the separation of tantalum from niobium, this being the first application of tannin to the quantitative separation and determination of the earth-forming elements. Whilst that method is quite sound, there is, no doubt, some justification for the criticism that the original directions are rather involved; further, some of the recorded errors are unduly and unnecessarily high (we did not suppress any of the less favourable results); again, compensation of errors may have contributed to the apparent success of some of the tests. As it happened, the most difficult separation problem capable of being solved by the application of tannin was also the first to be studied; subsequent adaptation of the new procedure to other separations (*e.g.* XXIII, Analyst, 1932, **57**, 550) led to an improved technique. This paper gives a concise description of the standardised fractionation process, as well as some examples of its practical application, which should prove a further help to those desiring to become familiar with the operation.

Rationale of Method.—It is assumed that the operator is acquainted with the chemistry of the process. Suffice it to recall that tantalum and niobium are completely precipitated by excess of tannin from their oxalate solution on neutralisation with ammonia, but by carefully regulated addition of the two reagents it is possible to effect a separation, tantalum being precipitated from slightly acid solution. The tantalum-tannin complex is yellow, the niobium complex red; co-precipitation of niobium with the tantalum is indicated by the orange colour of the tannin precipitate. Fractional precipitation is unavoidable, because the tantalum cannot be quantitatively precipitated without considerable contamination with niobium if the tantalum concentration is lower than the niobium concentration.

The standardised procedure furnishes three fractions, namely, (i) a niobium-free tantalum fraction (yellow precipitates); (ii) a mixed or intermediate fraction (orange to red precipitates); and (iii) a niobium filtrate free from tantalum. (With low Ta : Nb ratios, a yellow precipitate will not be obtained in the first fractionation.)

Quantitative separation is achieved by *systematic re-treatment of the mixed or intermediate fraction*; this is fractionated as before, yielding another three fractions, the intermediate of which is fractionated in its turn (and so on, if necessary). All the yellow, pure tantalum precipitates are ignited together; the pure niobium filtrates are combined.

After one or two fractionations the intermediate fraction will have been reduced to something of the order of 0·02, or even less than 0·01, grm. If the operations are properly performed, the total error will be confined to that incurred in the final treatment of the last intermediate fraction. At that stage it is necessary, in order to counteract incomplete recovery of the tantalum, to produce a slightly niobiferous final tantalum fraction (*i.e.* pale orange precipitate). This conforms with the principle I have previously applied in the determination of platinum: "If a substance cannot be precipitated quantitatively in one operation without undue contamination, it may be feasible to obtain it in two fractions. The first or major fraction should be pure. The minor fraction completes the precipitation; it is not pure, but, if sufficiently small, it renders the error negligible for practical purposes." (ANALYST, 1930, 55, 550.)

Reagents.—Potassium bisulphate, silica-free. Ammonium oxalate, saturated solution. Ammonium chloride, saturated solution. Tannin, freshly prepared 2 per cent. solution. *N* ammonia. Wash-liquor for tannin precipitates: 2 per cent. ammonium chloride. All reagents should be free from calcium salts.

Apparatus.—Tared silica crucible *s* for bisulphate fusion. A pair of fractionation beakers (600 c.c.; smaller size for end-fraction). Tared porcelain crucible, *p*, for tantalum precipitates. Squat beaker *B* (800 c.c.), for niobium filtrates. Apparatus for suction filtration (platinum or hardened paper cone). Whatman filters No. 40, 12·5 c.c. and smaller. For the smaller precipitates, simple filtration through Whatman No. 41 paper. Filter pulp. Burette for tannin (cf. *Manipulation, ignition, and leaching of tannin precipitates:* XIX, ANALYST, 1931, **56**, 308).

Notation.—The precipitates obtained in the first fractionation are designated, in succession, P^1, P^{1a}, P^{1b}, P^{1c}; those obtained in the second fractionation (*i.e.* re-treatment of the first intermediate), as P^2, P^{2a}, P^{2b}; those from the third fractionation (re-treatment of the second intermediate) as P^3, P^{3a}, P^{3b}, etc.

The Separation.—The mixed pentoxides (0·2 to 0·3 grm., or more if poor in tantalum) are fused with potassium bisulphate in the crucible *s*, and the product is dissolved in hot ammonium oxalate solution (75 to 100 c.c.). Any small residue is filtered off and re-treated, and the resulting solution (filtered if necessary) is added to the main portion.

FIRST FRACTIONATION.—The boiling solution (250 c.c.) is cautiously titrated with tannin reagent; if this produces a yellow coloration, enough tantalum is present to yield a yellow (niobium-free) P^1, provided the addition of tannin is interrupted before the yellow tint deepens to orange; see (*a*). If, however, an orange or red coloration is produced, P^1 will contain niobium as well as tantalum; see (*b*).

(*a*) *The Coloration is Yellow.*—Four precipitates are produced in the first fractionation (or three if P^{1a} is orange instead of yellow):

Tantalum fraction: P^1 (main fraction), P^{1a}.
Intermediate (mixed) fraction: P^{1b}, P^{1c}.

The four precipitations are done in one day, filtration of P^{1c} taking place the next morning.

P^1 (*yellow*): the gradual addition of tannin is continued while the boiling liquid is being stirred; with high tantalum contents a yellow precipitate will be formed. Any orange coloration appearing at the point of incidence of the reagent is made to disappear by agitation. The addition of tannin is interrupted before any permanent colour-change takes place; in no case is more than 50 c.c. of tannin reagent added. Complete flocculation is brought about by addition of 30 to 50 c.c. of saturated ammonium chloride solution; partial neutralisation with N ammonia to induce precipitation is hardly ever necessary in the case of P^1. The solution is boiled gently for 5 to 10 minutes, and left on the water-bath for half an hour. The precipitate P^1 is collected, well washed (return to precipitation beaker), and ignited in crucible *p*.

P^{1a} (*yellow*): the filtrate from P^1 is boiled down while the precipitate is being washed; the total volume of filtrate and washings is kept approximately constant during each fractionation. The boiling solution is cautiously treated with N ammonia until a permanent cloudiness appears, then slowly titrated with tannin, being agitated meanwhile. The bulky P^1 having been eliminated, it is usually possible, by observation of the delicate colour changes, to obtain an additional yellow fraction P^{1a}. This is treated, as before, by boiling and digestion on the water-bath. If yellow, the washed P^{1a} is added to P^1. If, however, P^{1a} appears orange after settling on the water-bath, the gradual addition of N ammonia and tannin should be continued; this will produce a larger precipitate of decided orange colour, *i.e.* the first intermediate precipitate P^{1b}.

P^{1b} (*orange*): the concentrated filtrate from the yellow precipitate P^{1a} is boiled, stirred, treated with N ammonia until slightly cloudy, and titrated with tannin until a deep orange precipitate is produced. The ignited P^{1b} should amount to 0·01 to 0·02 grm. After boiling, digestion on the water-bath, and filtration, the washed precipitate is ignited in crucible *s*.

P^{1c} (*red*): the concentrated filtrate from P^{1b} is treated exactly as the preceding filtrate, but the red precipitate P^{1c}, after digestion on the water-bath, is set aside overnight before filtration. The washed P^{1c} is added to P^{1b}; the tantalum-free filtrate F^{1c} is concentrated in beaker *B*.

The precipitation of the intermediate fraction in two portions is always advisable, as total precipitation of the tantalum has not necessarily taken place when incipient precipitation of niobium becomes evident: at low tantalum and high niobium concentrations the two stages overlap. If P^{1b} is orange at first and reddens with continued addition of ammonia and tannin, whilst P^{1c} is decidedly reddish at the time of its formation, it may safely be inferred that total precipitation of tantalum has been achieved.

Each fraction is weighed to the nearest mgrm.; the colour and weight of the precipitates are recorded as important guides, together with the amount of tannin added.

(*b*) *The Coloration is Orange to Red.*—No tantalum fraction will be obtained. The mixed fraction, containing all the tantalum and some niobium, is produced in two portions, P^1 and P^{1a}, which correspond with P^{1b} and P^{1c} of the preceding case.

P^1 (*orange to red*): the addition of tannin to the boiling solution is regulated from a minimum of 10 c.c. (for low Ta : Nb ratios) to about 20 c.c. The precipitate is flocculated by addition of 30 c.c. of the ammonium chloride solution, if necessary a little *N* ammonia, boiling, and digestion on the water-bath. It is collected, washed, and ignited in crucible *s*.

P^{1a} (*red*): the concentrated, boiling filtrate from P^1 is treated with a little *N* ammonia, followed by tannin; a red precipitate should be obtained, yielding about 0·02 grm. of ignited oxide. The liquid is set aside overnight; P^{1a} is collected, washed, and added to P^1. The tantalum-free filtrate, F^{1a}, is concentrated in beaker *B*.

Second Fractionation.—The weighed intermediate fraction ($P^{1b} + P^{1c}$) (case *a*), or the mixed fraction ($P^1 + P^{1a}$) (case *b*), is fused with bisulphate, and the product dissolved in ammonium oxalate solution.

The second fractionation is exactly like the first. The operations take place on a reduced scale; the manipulative details remain identical. The boiling oxalate solution is cautiously titrated with tannin, which produces either a yellow (*c*) or, if the tantalum content is very low, an orange to red (*d*), coloration.

(*c*) *Yellow Coloration.*—Properly performed, the first fractionation of a tantalum-rich mixture gives a small intermediate fraction ($P^{1b} + P^{1c}$), the niobium-content of which is sufficiently low (see example *A* below) to enable the operator to complete the separation at this stage. The directions will be found under "*Final fractionation.*"

If, on the other hand, the original oxide mixture contained substantial quantities of both oxides, then the intermediate fraction will be heavier (example *c*), and its re-treatment will constitute the penultimate fractionation. Three precipitations are carried out (four are hardly necessary):

P^2: yellow. Ta fraction; to crucible *p*.

P^{2a}: yellow or orange (see below).

P^{2b}: orange to red. Mixed fraction; to crucible *s*.

The precipitate P^{2a} is disposed of according to its colour: if yellow, it is added to P^2; if orange, to P^{2b}. It is not at all uncommon to obtain a yellow P^{2a}. The tantalum-free filtrate F^{2b} is added to beaker *B*.

(*d*) *Orange to Red Coloration* (very low tantalum content).—Another mixed fraction, in two portions, will have to be produced, exactly as in the first fractionation (case *b*):

P^2: orange to red. To crucible *s*.

P^{2a}: red. Collected next day; to crucible *s*.

The tantalum-free filtrate F^{2a} is added to beaker *B*. In the present case, ($P^2 + P^{2a}$) should not be subjected to final fractionation without an intervening third fractionation, which must yield a yellow head-fraction P^3.

FINAL FRACTIONATION.—As explained under *Rationale*, the final tantalum fraction to be produced should be slightly niobiferous; hence the mixed fraction submitted to final fractionation should be as small as possible, and comparatively low in niobium. When to undertake the final fractionation is a matter for the operator's judgment, which must be based on each occasion on the colour as much as on the weight of the intermediate fraction to be treated. The examples given in the Experimental Part are perhaps the best practical guide for this part of the process.

The intermediate fraction having been dissolved as before, the boiling solution (50 to 100 c.c.) is treated with tannin until a pale orange coloration is obtained. Flocculation is induced by 10 to 20 c.c. of ammonium chloride solution and a few drops of *N* ammonia. Should the coloration be yellow, the final fraction can be obtained in two portions, a yellow precipitate first, and a pale orange one in the filtrate therefrom.

DETERMINATION OF THE TANTALUM.—The weight of the tantalum fraction must always be corrected for adsorbed salts, silica (filter ash), and probably titania. The combined ignited precipitates are lixiviated with 2 per cent. hydrochloric acid, collected, strongly ignited, and weighed. The oxide is then fused with bisulphate, the product is dissolved in ammonium oxalate, and the slight residue is collected, washed, ignited, and weighed as SiO_2. The cold oxalate filtrate is treated with dilute sulphuric acid and hydrogen peroxide, and the titania, if any, is determined colorimetrically. The sum of SiO_2 and TiO_2, subtracted from the weight of the leached precipitate, gives the net weight of Ta_2O_5.

DETERMINATION OF THE NIOBIUM.—This oxide may be taken by difference. For a direct determination, the combined niobium filtrates are boiled with 0·5 to 1 grm. of tannin and a small excess of ammonia. The ignited (generally ferruginous) precipitate is fused with bisulphate, the mass is dissolved in ammonium oxalate, and the solution is freed from silica by filtration; the filtrate is neutralised with *N* ammonia and diluted with an equal volume of saturated ammonium chloride solution, and the niobium is precipitated with tannin, as directed in Section XIX, D (*loc. cit.*). The ignited precipitate is leached, weighed, and tested for titania like the tantalum precipitate.

EXPERIMENTAL

Four examples of the application of the process are given. The composition of the mixed oxides treated is represented by the following $Ta_2O_5 : Nb_2O_5$ ratios:—4:1 (*A*); 1:4 (*B*); 3:2 (*C*); and 1:300 (*D*).

Example A.—Taken: 0·2023 grm. of Ta_2O_5, 0·0550 grm. of Nb_2O_5.

Tannin solution	Fractionations		Gross weight of precipitates	
c.c.	First	Second	Mixed fractions Grm.	Ta_2O_5 fractions Grm.
50	P^1, yellow			0·1866
20	P^{1a}, yellow			0·0144
5	P^{1b}, orange	re-treated	0·0070	
5	P^{1c}, red		0·0040	
18		P^2, yellow		0·0042
3		P^{2a}, pale orange		0·0008
			Gross weight of Ta_2O_5 fraction	0·2060
			Less leaching loss 0·0030 grm., SiO_2 0·0012 grm.	0·0042
			Net Ta_2O_5 found	0·2018

Mixtures rich in Ta_2O_5 provide the simplest case for separation. More than 90 per cent. of the Ta_2O_5 is recoverable as P^1.

Example B.—Taken: 0·0516 grm. of Ta_2O_5, 0·2006 grm. of Nb_2O_5, 0·0012 grm. of TiO_2.

Tannin solution	Fractionations			Gross weight of precipitates	
c.c.	First	Second	Third	Mixed fractions Grm.	Ta_2O_5 fractions Grm.
20	P^1, orange	re-treated		0·0624	
5	P^{1a}, red			0·0160	
10		P^2, yellow			0·0422
3		P^{2a} (see below)	re-treated	0·0140	
1		P^{2b} reddish		0·0144	
5			P^3, yellow		0·0114
1			P^{3a}, pale orange		0·0034
				Gross weight of Ta_2O_5 fraction	0·0570
				Less leaching loss 0·0016 grm., SiO_2 0·0027 grm., TiO_2 0·0009 grm.	0·0052
				Net Ta_2O_5 found	0·0518

The separation was satisfactory, although the Ta_2O_5 : TiO_2 ratio of 43 is rather low (*cf.* Section XI, ANALYST, **1928**, **53**, 266). We were over-cautious in our earlier paper when we stated that the titania should "not much exceed 1 per cent. of the tantalic oxide to be determined"; it appears from this test that 2 per cent. does no harm.

The appearance of P^{2a} was rather deceptive: it was intended to be added to P^2, but, when packed on the filter (which is always the safest way to judge of the colour of the precipitates), it appeared too impure for a tantalum fraction; hence it was re-treated. As will be shown in a subsequent paper, tungsten acts like titanium in affecting the colour of the tantalum precipitate.

Example C.—Analysis of a pure preparation of mixed pentoxides used in test analyses (Section VIII, ANALYST, 1927, **52**, 512). Taken: 0·3300 grm.

Fractionations			Weight of precipitates	
First	Second	Third	Mixed fractions Grm.	Ta_2O_5 fractions Grm.
P^1, yellow				0·1759
P^{1a}, orange P^{1b}, red	re-treated		0·0537	
	P^2, yellow			0·0208
	P^{2a}, yellow			0·0027
	P^{2b}, orange	re-treated	0·0072	
		P^3, yellow		0·0016
		P^{3a}, pale orange		0·0015
		Net weight of Ta_2O_5 fraction		0·2025

Ta_2O_5, 61·4 per cent.; Nb_2O_5 (by difference), 38·6 per cent.

In this older analysis the amount of tannin used was not recorded. The net weights of the tantalum precipitates are given; P^1 was purified by itself by the usual lixiviation process. The figures for the other four tantalum fractions represent the weight less filter-ash.

Example D.—Analysis of a preparation of niobic oxide:—Taken: Two 1-grm. portions, fractionated as in Section V (ANALYST, 1925, **50**, 496). Five successive treatments.

Tannin solution c.c. per portion	Fractions		Grm.
10	P^1 (red), combined, from two portions		0·565
10	P^2 (red)		0·122
5	P^3 (orange) 0·0250; P^{3a} (red) 0·0110.	ΣP^3	0·0360
5	P^4 (pale orange) 0·0066; P^{4a} (orange) 0·0056.	ΣP^4	0·0122
4	P^5 (yellow) 0·0045; P^{5a} (pale orange) 0·0029.	ΣP^5	0·0074

The net weight of the Ta_2O_5 fraction is 0·0074 grm., the impurities having been filtered off after solution of the bisulphate melt of ΣP^4 in ammonium oxalate. Hence the Ta_2O_5 content of the preparation is 0·37 per cent. Mr. A. R. Powell, having worked quite independently, and in ignorance of my result, reported 0·32 per cent. of Ta_2O_5 in the material.

It only remains to be added that the coloration of the tannin filtrates is of no diagnostic importance in the fractionation: in fact, it will be found that the filtrates obtained by the application of the revised procedure are colourless, or nearly so. I am now satisfied that the straw-yellow colour discussed in the earlier paper was caused by excess of tannin. An orange or reddish filtrate indicates incomplete flocculation, which is easily corrected by addition of more ammonia or tannin. Ammonium oxalate solution, applied in the earlier work as a means for depressing the hydrogen ion concentration, has proved to be unnecessary, and its use has been discontinued.

SUMMARY.—An improved procedure for the separation of tantalum from niobium, based on fractional precipitation of the oxalate solution by tannin, is described. Four instances of the application of the method to mixtures of the two oxides in various proportions are recorded.

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An Improved Micro-Apparatus for the Determination of Molecular Weight

By A. F. COLSON, B.Sc., A.I.C.

(*Read at the Meeting of the North of England Section, October* 15, 1932)

WHEN using the macro-apparatus devised by Menzies and Wright (*J. Amer. Chem. Soc.*, 1921, **43**, 2314) for the determination of molecular weight by the ebullioscopic method, it is necessary to fulfil the following conditions in order to obtain reliable results:—(1) The upper bulb of the differential thermometer must be adequately bathed by the condensed solvent. (2) The apparatus (including the flame used to boil the solvent) must be properly shielded from air-draughts. (3) The volume of the solvent at its boiling-point must be determined in such a manner that no appreciable drainage of condensate from the inner walls of the apparatus can take place before the required reading of the volume is made.

The first of these conditions is satisfied to a certain extent in the macro-apparatus in the following manner:—Two short wires are attached to the differential thermometer at a point above the upper bulb. When the thermometer is in use these wires make contact with the inner wall of the condenser, and serve to direct a stream of condensed solvent towards the neighbouring bulb of the thermometer.

To fulfil the second condition to some extent, the apparatus is provided with a loosely-fitting glass cylinder. This cylinder is inside the apparatus and acts as a screen to the thermometer.

The third condition is the most difficult one to satisfy. An accurate determination of the volume of the solvent at its boiling-point cannot be made by removing the flame from under the boiling vessel, and reading off the volume as soon as the surface of the liquid has become sufficiently quiescent. This method fails because the heat retained by the vessel containing the solvent is sufficient to keep the liquid feebly boiling for two or three seconds after the flame has been removed. During this short period sufficient condensed solvent drains down from the walls of the apparatus to make an accurate reading impossible.

Menzies and Wright (*loc. cit.*) determined the volume by removing the flame and cooling the solvent in a beaker of cold water immediately before taking the reading.

If these three operations are carried out in the shortest possible time a fairly satisfactory determination of the volume can be made, but the method is undoubtedly inefficient and leaves much room for improvement.

The efficiency of the micro-apparatus recently devised by Milner and Smith (*Mikrochemie*, 1931, **3**, 117) is similarly impaired by this imperfection in the method of measuring the volume of the solvent.

By the adoption of an entirely different method of heating the solvent it has been found possible to construct an apparatus which is free from the defect common to the macro- and micro- forms referred to above. This improved micro-apparatus is described below.

The solvent is heated electrically. A spiral of thin platinum wire, wound on a core of glass rod, about 1 mm. in diameter, constitutes the heating element, A, which is immersed in the solvent. The ends of the coil are joined to two platinum leads which are sealed through the walls of the vessel V and carry the terminals B^1 B^2. The resistance of the spiral is about 3·0 ohms, and the current required to heat the solvent sufficiently is about 2·8 amps.

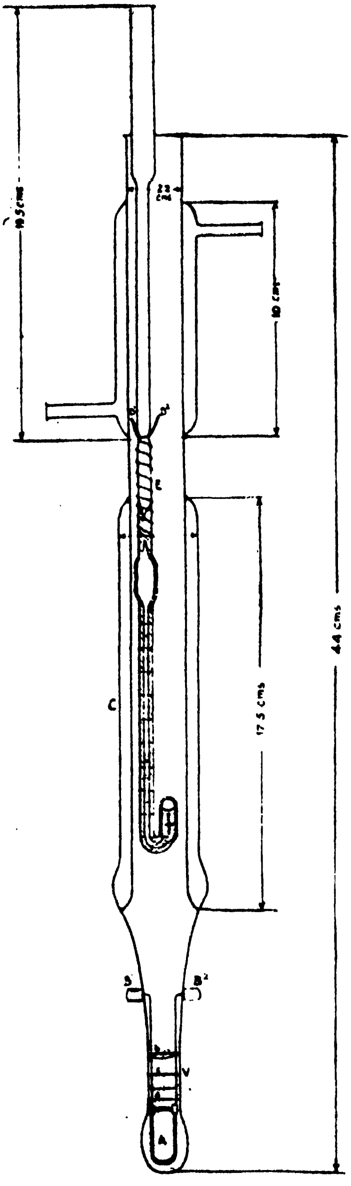


Fig. 1

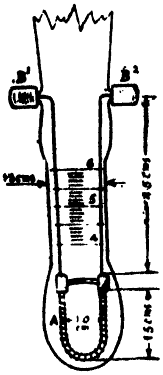


Fig. 2

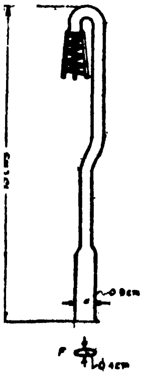


Fig. 3

The copper spiral E, used by Milner and Smith (*loc. cit.*), has been adopted because it produces a more efficient bathing of the upper bulb of the differential thermometer than is possible with the two wires D^1 D^2 alone. This spiral is joined to the junction of the wires D^1 D^2, and extends to the bulb of the thermometer.

The vacuum jacket, C, which is also a feature of Milner's and Smith's apparatus, affords better protection from air-draughts than the internal vapour jacket formerly employed. The Cottrell pump, F, has been very slightly modified, as shown in Fig. 3, in order that the lower end may pass easily between the platinum leads in the vessel V.

Since the apparatus is a modification of the macro-form devised by Menzies and Wright (*loc. cit.*), the method of making a determination of molecular weight is essentially the same as that given in their paper.

A few special points peculiar to the improved micro-apparatus must be mentioned.

To determine the volume of the solvent at its boiling-point the current is stopped, and the required reading is taken at once. The solvent becomes quiescent and in a suitable condition for measurement so soon after the current is stopped that the cooling, which is necessary in all the types of apparatus hitherto used, is not necessary in this improved apparatus. A number of measurements can be made very easily and quickly, the agreement between them being of the order of 0·02 ml. The substance of which the molecular weight is required is introduced into the solvent in a glass cup, 0·4 cm. in diameter and 0·4 cm. deep.

The volume of solvent used should not be more than about 6 ml. Two further advantages afforded by the use of the apparatus here described are:—(1) The source of heat is not susceptible to air-draughts. (2) The height to which the solvent rises in the condenser—and consequently the volume of solvent remaining in the boiling vessel—can be fixed by keeping the current constant.

In order that the readings registered by the differential thermometer shall remain steady during a determination, it is important to ensure that the wires D^1 D^2 make contact with the inner wall of the condenser at points not appreciably less than 1 cm. below the upper edge of the column of condensed solvent.

The table below shows some results obtained with coumarin (mol. wt. = 146) in benzene as solvent.

Weight of coumarin Mgrms.	Volume of benzene Ml.	Boiling-point of benzene °C.	Rise above zero reading Mm.	Conversion factor	Ebullioscopic constant	Molecular weight
10·599	5·05	80·8	9·4	0·004833	32·0	148
8·369	5·23	80·5	6·9	0·004884	,,	150
15·647	5·23	,,	13·7	,,	,,	143
5·921	5·70	80·2	4·6	0·004935	,,	147
13·459	5·70	,,	10·3	,,	,,	149

I wish to thank the Directors of Imperial Chemical Industries, Limited, for permission to publish the results of this work.

Sediments in Ink and in Writing

By C. AINSWORTH MITCHELL, D.Sc., F.I.C., and T. J. WARD

(*Read at the Meeting, May* 4, 1932)

For several years we have been studying, more or less independently, the nature of the sediments which form in ink and their significance in writing.

Normal Sedimentation in Ink Vats.—All inks made from galls, copperas, dye, and acid are allowed to stand for several weeks at least, in order that the vegetable débris and the more insoluble iron-tannin compounds may subside. The sludge at the bottom of the vat varies in composition, but usually contains a considerable proportion of the blue dyestuff, which has been carried down mechanically, and, when oxalic or tartaric acid has been used as the stabilising agent, it will also contain insoluble oxalates or tartrates. The amount of iron in the dry deposit has been found to range from less than 5 per cent. to over 27 per cent., as is shown by the following partial analyses of actual deposits, dried at 100° C.

	I Per Cent.	II Per Cent.	III Per Cent.	IV Per Cent.	V Per Cent.
Mineral matter	17·51	49·04	9·12	10·12	14·20
Organic matter	82·49	50·96	90·88	89·88	85·80
Iron in deposit	13·12	27·35	6·28	4·76	7·06
Iron in mineral matter	74·92	55·77	68·85	45·68	49·71

Special interest attaches to No. V, since it is a deposit from a vat of gallic acid ink. In one experiment, on a large scale, in which the sediment was separated by centrifuging, the moist solid material contained 0·38 per cent. of the blue dye.

If the ink is drawn off before sedimentation is complete, the process will continue in the bottle, and eventually a very fine deposit will be thrown down and will spoil the appearance of the ink. Writing done with ink containing such deposit will differ in appearance under the microscope from that done with a normal clear ink, as may be seen in Pl. I, 1 and 9.

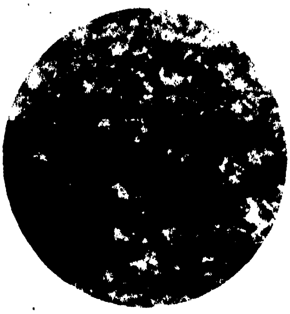
Abnormal Sedimentation.—If the proportion of iron to the tannin has not been correctly calculated to yield a soluble iron tannate which will oxidise but slowly, an insoluble iron tannate will be rapidly formed, and, except for the iron gallate present, the ink will be decolorised.

For example, in experiments in which that remarkable glucose-free gallotannin, previously described (Analyst, 1923, **48**, 7, 328), was used, the following typical results *inter alia* were obtained. For practical purposes the 10·1 per cent. of gallic acid in this tannin may be ignored, since it has little effect upon the calculations.

Gallotannin Grm.	Iron sulphate Grm.	Ratio of tannin to iron		Effect
0·1	0·1	10	2	Precipitation in 5 days
0·1	0·05	10	1	Precipitation in 10 to 15 days
0·1	0·025	10	0·5	Stable for six weeks

PLATE I

1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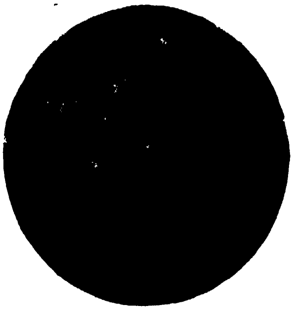
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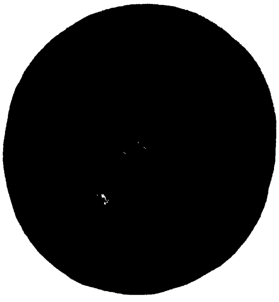
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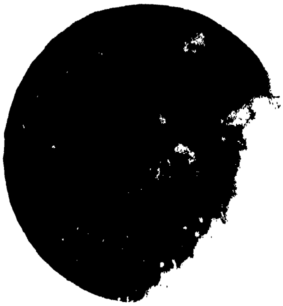
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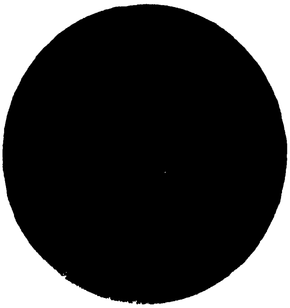
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(1) Normal sediment.
(2) Excess of tannin.
(3) Excess of iron.
(4) Excess of gallic acid.
(5) Frozen ink.
(6) Effect of pen left in ink.
(7) Mould hyphae.
(8) Effect of alkaline glass.
(9) Oxalic acid sediment in vat.
(10) Sand in letter, 1842.
(11) Sand in book, 1840.
(12) Pumice in letter, 1837.

PLATE II

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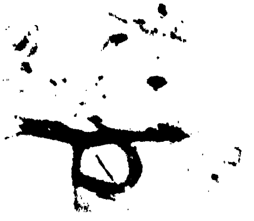
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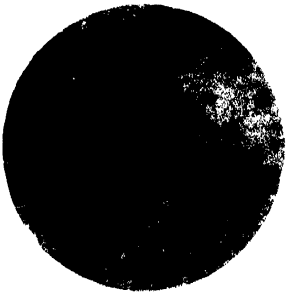
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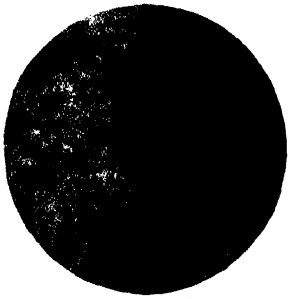
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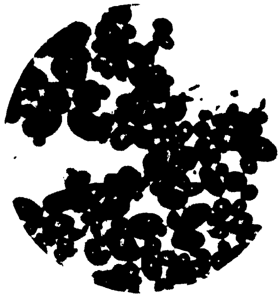
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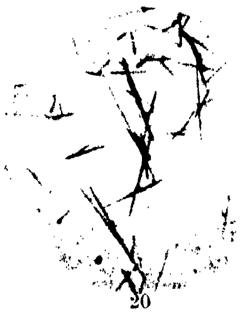
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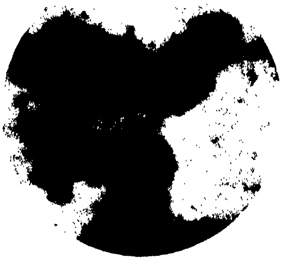
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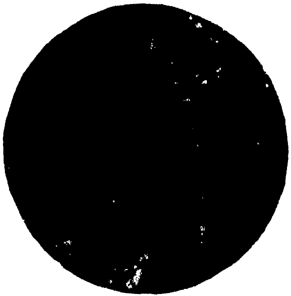
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(13) Brown sand in letter, Cairo, 1932.
(14) Plant débris in letter, June, 1917.
(15) Plant débris in letter, July, 1917.
(16) Plant hair in letter, 1902.
(17) Moth scales in letter, 1894.
(18) Moth scales, experimental.
(19) Potato starch in letter, 1904.
(20) Asbestos in letter, 1930.
(21) Calcium sulphate, laboratory notebook, 1896.
(22) Effect of chalk in ink.
(23) Sediment in laboratory notebook, 1896.
(24) Blotting paper fibres on letter, 1932.

Hence, the ratio of iron to tannin should be about 5:100, and if there is much deviation from this proportion in either direction, precipitation may occur either in the vat or, later, in the ink-bottle.

The effect of excess of either ingredient in the ink may appear in writing done with it. If there is excess of iron, the ink will stain the paper in a uniform bluish-green layer (Pl. I, 3), in which the usual large masses of black pigment will not appear, whereas if there is an abnormal excess of tannin the accumulations of pigment will appear as large black irregular clots (Pl. I, 2).

SEPARATION OF GALLIC ACID.—Occasionally, a crystalline film may form on the surface of the ink in a closed bottle and lead to complaints which will puzzle an ink-maker, since he is confident that no change has been made in the formula used in the preparation of an ink which has previously proved satisfactory. The explanation of the trouble depends upon the fact that the solubility of gallic acid is so small that an ink, especially one prepared from tannic acid (gallotannin), may become saturated with gallic acid at a relatively high temperature, and if the bottle is then exposed to a somewhat lower temperature, the gallic acid will separate in minute crystals on the surface.

Solubility of Gallic Acid.—The following table shows the solubility of pure gallic acid (dried at 100° C.) in distilled water at various temperatures. The gallic acid used contained 10·3 per cent. of water, and its purity, determined colorimetrically by comparison with pyrogallol (ANALYST, 1923, **48**, 2), was 100 per cent. (m.pt., 241° C.). When this gallic acid was heated with boiling water until a homogeneous liquid was obtained, the solution contained 48·71 per cent. (by weight) of gallic acid. At other temperatures the percentage solubility (w/w) was as follows:

Temperature	43°C.	32°C.	28°C.	21°C.	15°C.	7·5°C.	5·5°C.	5·0°C.	3°C.
Solubility	3·39	2·61	2·17	1·72	0·91	0·76	0·74	0·73	0·59

Commercial Gallotannins.—The following analyses, which are typical, are those of two commercial gallotannins, the first of which produced a crystalline film on the ink made from it, whilst the other did not. The tannin and gallic acid were determined by the colorimetric method (*loc. cit.*).

	A Per Cent.	B Per Cent.
Water	9·9	6·2
Total tinctogenic value (in terms of gallic acid)	[64·8 per cent.]	[62·0 per cent.]
Gallic acid	39·7	12·4
Gallotannin	25·1	49·6
Non-tinctogenic substances	25·3	31·8

The consignment A contained an exceptionally high proportion of gallic acid, with the result that the ink must have reached its saturation point for that acid at the ordinary temperature (15·5° C.), and, when chilled, readily produced a crystalline film.

The appearance of writing in ink from which the gallic acid has crystallised is characteristic. (Pl. I, 4.)

FROZEN INK.—A condition under which an ordinary blue-black ink might appear to be a mixture of a writing- and a copying-ink is when it has been frozen and is in the state of thawing. One would hardly anticipate that anyone would be so unreasonable as to write with a half-thawed ink and then to complain of the result, and yet on several occasions ink-manufacturers have had to investigate such complaints.

If an ordinary iron-gall blue-black ink is frozen into a solid disc, a fractionation occurs. The edges of the mass are colourless, whilst the iron tannate and dye become concentrated in the middle and lower parts of the disc. When the part which thaws first beneath the mass is decanted it will be found to contain approximately twice as much blue dye as the original ink, whilst the iron tannate and other constituents will show a corresponding increase. With a gallic acid ink the separation into fractions is much less pronounced than with an iron-gall ink. The following figures give some idea of the fractionation that occurs.

FROZEN INKS

	Original ink Per Cent.	Part first thawing Per Cent.	Residue thawing last Per Cent.
Iron-gall ink.			
Total solids	3·60	6·39	1·19
Mineral matter	0·56	0·82	0·24
Iron	0·28	0·47	0·16
Gallic acid ink.			
Total solids	3·34	4·24	2·16
Mineral matter	0·38	0·66	0·30
Iron	0·28	0·41	0·14

If a partly-thawed ink is used for writing, the portion near the bottom of the ink-bottle will produce the effect of a copying-ink, that is to say, will show an increased deposit of blue and black pigments, and may appear iridescent in places. It may also appear to contain spicules (Pl. I, 5), although, in reality, these are cavities from which the ice-crystals have melted. On the other hand, the upper part will be deficient in dye and iron tannate, and will produce paler writing than the bottom fraction.

EFFECT OF PEN LEFT IN INK.—One of the most frequent causes of the decomposition of ink in ink-wells is the practice of leaving the pen in the ink. The acid in the ink soon dissolves the iron of the nib, and when an excess of iron in proportion to the tannin is reached, an insoluble tannate is precipitated.

Many years ago one of us based a crude test for the acidity of inks on the determination of the loss in weight by a pen-nib immersed in the ink, and the method was subsequently officially adopted (without acknowledgment) in the United States. The test is still a useful one for comparative purposes, as is shown by the following results recently obtained by leaving weighed pen-nibs for 20 days in 10 c.c. of different inks, and subsequently cleaning, drying, and weighing the nibs.

	Loss in weight of nib	Original ink			Filtrate from deposit		
		Total solids	Mineral matter	Iron	Total solids	Mineral matter	Iron
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
A. English ink	10·99	3·25	0·42	0·20	2·27	0·8	0·46
B. Ditto	12·05	4·00	0·84	0·35	2·17	1·05	0·76
C. Japanese ink	12·75	5·28	2·02	0·59	3·83	2·47	0·80

Writing done with ink which has been decomposed by a pen-nib appears, in a photomicrograph, very similar to that done with an ink containing an excess of copperas. (Pl. I, 6.)

WATERED INK.—Another common cause of sediments in ink is the practice, sometimes adopted in cottages, of eking out the ink by the addition of water. Frequently the deposit in an ink-well has become largely insoluble, and the addition of water not only reduces the colour of the soluble dye, but also leaves particles of sediment. The effect of such dilution on writing is usually quite distinct from that of a blotted ink, which will generally show a pale uniform ground, without the solid particles to be seen in watered ink.

DEPOSITS IN MIXED INKS.—The admixture of two inks of different character may cause sediments to form, and these may be conveyed into the writing. This was the explanation of the abnormalities in the case of *Skelton* v. *Hawes*, in which a will had been written in a mixture of three different inks, and the strokes of the writing showed not only particles of sediment, but also different colours in different parts of the signatures (see ANALYST, 1932, 146).

Attempts to age an ink artificially may also sometimes be detected by an examination of the writing, as happened in a case in which a clerk had falsified a ledger by writing up the entries in a mixture of ordinary ink and Indian ink. The addition of a drop of dilute sodium hypochlorite to one of the characters at once revealed the fraud, for the particles of lamp-black derived from the Indian ink remained unbleached.

Accidental dipping of the pen into the wrong bottle of ink may afford useful evidence in the writing. An instance of this occurred in the case of *Rex* v. *Thurburn*, in which the defendant was charged with writing anonymous letters. An admitted document in the case was a series of caricatures drawn in artist's black ink, and the fact that two of the printed characters in the middle of the writing on an anonymous card were in the same kind of ink indicated that the writer of that card had accidentally dipped the pen into a bottle of that ink.

In a more recent case (*Riddle and Holder* v. *Midland Bank*, 1932) there were on a document two signatures, the authenticity of which was not disputed, although there was a sharp conflict of evidence as to the place where they were signed, the plaintiffs contending that they were signed separately in Banbury, and the defendants that they were signed at the same time in a bank manager's office. The upper signature was written in an ordinary blue-black ink, whilst in the other the dye of the ink formed a pale greyish-violet ground on which the black pigment was distributed in irregular spots. The microscopical appearance was consistent with that of an ink in which the blue dye had faded and the black pigment had formed a sediment in the ink-well (Fig. 25). This agreed with the story of the plaintiffs that the second signature had been signed with an old fountain-pen upon the nib of which the ink was encrusted, and that this had been dipped into a dirty ink-pot at a farm-house.

The defendants accounted for the abnormal appearance of the second signature by the hypothesis that the pen had been accidentally dipped into a bottle of copying-ink standing open on the desk in the bank manager's office. Experiments, however, showed that the writing had none of the characteristics of a mixture of copying-ink and ordinary blue-black ink. These mix well and do not form a sediment, but the writing shows an increase of lustre due to the larger amount of aniline dye in the copying-ink. The signature in question, so far from showing an increase in dye, contained very much less than writing done with an ordinary blue-black ink.

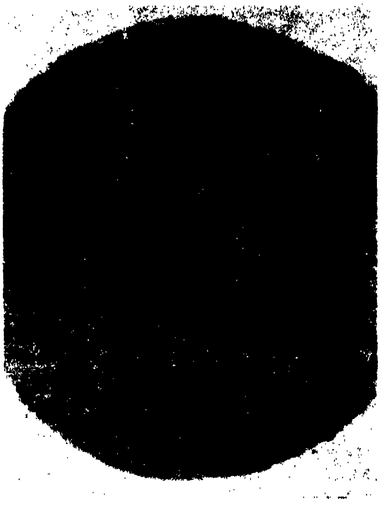

Fig. 25

Full-stop in signature, showing black deposit on grey back-ground × 50

Effect of Alkaline Glass.—It has already been demonstrated (Analyst, 1921, 46, 129) that ink may be completely decomposed by alkali dissolved from badly-made glass ink-bottles, and the appearance of writing in such ink is quite characteristic (Pl. I, 8), and not to be confused with writing in other forms of decomposed ink.

Moulds in Ink.—In former times bay-salt was added to ink to prevent it from becoming hoary,[*] *i.e.* turning grey, through the growth of mould. In modern inks carbolic acid (or, less frequently, salicylic acid) is used for the same purpose. This precaution, however, is not always effective, for, occasionally, the ink in bottles which had been closed with a cork infected with mould will develop a growth which will eventually cause the ink to decompose, and infection with mould may also occur in ink exposed to the air in an ink-well.

This growth is not surprising, for, among the results recorded by Thom (*The Penicillia*, p. 90) are those of Sabalitscha and Dietrich (*Disinfektion*, 1926, II, 67), who found that it required 0·14 per cent. of salicylic acid and 0·014 per cent. of phenol or thymol to inhibit the growth of a strain termed *Penicillium glaucum*. The optimum temperature for the growth of most species of *Penicillia* lies between 22° and 30° C. (Thom, *loc. cit.*, p. 85). Among the enzymes recorded as occurring in *Penicillia* sp. are amylase, cytase, diastase, maltase, lactase, and emulsin. Our experiments show that oxydase may be added to these, for the addition of a trace of mycelium powder from a strain of *Penicillium** caused a pronounced acceleration in the precipitation of iron tannate from a solution of gallotannin and ferrous sulphate. This is shown by the following results, which are typical of many:

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[*] Harr = Anglo-Saxon, *grey*,

	Tannin Grm.	Iron sulphate Grm.		Time of standing Days	Precipitate Grm.	Iron in precipitate Per Cent.
(*a*)	0·1	0·1	blank	3	0·049	6·7
(*b*)	0·1	0·1	inoculated	3	0·082	5·38
(*a*)	0·1	0·1	blank	8	0·071	13·6
(*b*)	0·1	0·1	inoculated	8	0·091	13·2
(*a*)	0·5	1·0	blank	11	0·2884	8·45
(*b*)	0·5	1·0	inoculated	11	0·3550	—
(*a*)	0·1	0·05	blank	18	0·045	5·6
(*b*)	0·1	0·05	inoculated	18	0·090	12·9
(*c*)	0·1	0·05	inoculated	16	0·097	—
(*a*)	0·1	0·025	blank	35	nil	—
(*b*)	0·1	0·025	inoculated	35	0·0264	6·09

Hence, in each instance, the precipitation of gallotannin by the iron was greatly accelerated by the presence of the mould, and in some of the tests it was practically complete (for the 10 per cent. of gallic acid in the tannin remained in solution in each set of tests), whilst only 50 to 60 per cent. had been precipitated in the absence of mould. Further work on this method of measuring oxidising activity is in progress.

A proof of the fairly common occurrence of moulds in the inks of some twenty-five to thirty years ago is afforded by the fact that fragments of hyphae and mould spores may be looked for and found in the inks on old letters (see Pl. I, 7).

POUNCES IN WRITING.—Long after the invention of blotting-paper the practice of using sand or other powder to dry writing was continued, and indeed is not altogether obsolete at the present day. Originally, the term "pounce" (*poncer*) was applied to a powder which was dusted on to parchment to make it take the writing. The so-called cuttle-fish "bone" (or "scuttle-bone") was commonly used for the purpose (cf. *The Purefoy Letters*,† p. 288), and subsequently the term was applied to the powders used to dry the writing. We are indebted to Mr. A. Lucas for a specimen of an Egyptian account book of 1767, the ink on which he described in a paper read before the Society (ANALYST, 1922, 47, 11). For drying this ink a mica powder had been used, and the deposit on the strokes is particularly apparent in certain additional notes on the page (see Fig. 26).

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* The *Penicillium* used in these experiments was kindly identified for us by Mr. Charles Thom, mycologist to the U.S.A. Department of Agriculture, as *P. terrestre, Jensen*, the name assigned to a group of strains rather than to a particular organism.

† *The Purefoy Letters*, 1735–1753. Edited by George Eland. 2 vols., with 28 plates. London: Sidgwick & Jackson, Ltd. Price 42s.

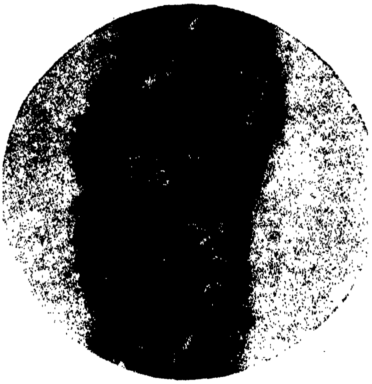

Fig. 26
Mica crystals on writing in Arabic account-book of 1767 × 25

Blotting-paper has now to a large extent replaced sand as the drying agent in the Courts of Cairo, but Mr. Lucas has kindly sent us a specimen of a brown sand still used for this purpose by an aged writer claiming to be 95 years old (Pl. II, 13).

Chemical analysis of this sand gave the following results:—Moisture, 0·08; sand, 57·38; insoluble organic matter, 9·52; chlorides (as sodium chloride), 32·49; soluble organic matter (by *diff.*), 0·53 per cent.

Microscopical examination and sedimentation* tests showed the material to consist of granite sand containing angular and rounded grains of quartz, orthoclase felspar, biotite mica, and magnetite (Fe_3O_4). The vegetable constituents included fragments of seed coats, stems, leaves, and hairs impregnated with sodium chloride. The small quantity of insect débris consisted of wing cases, legs and antennae, probably derived from small beetles.

Examination of specimens of iron-gall writing will also often reveal particles of the pounce still adhering to the surface. For example, very finely powdered pumice was detected in a letter written in 1837 (Pl. I, 11), and particles of sand were found in a letter dated 1842 (Pl. I, 10) and in a book of 1840 (Pl. I, 12). It is possible that the potato starch found in a letter of 1904 (Pl. II, 19) was derived from the use of farina for drying the writing.

Fibres of blotting-paper adhering to an ink may sometimes be distinctive, as is to be seen in the photomicrograph of the ink on an envelope received from Paris this year (Pl. II, 24).

EVIDENTIAL VALUE OF SEDIMENTS IN WRITING.—It is obvious that under certain conditions the presence of extraneous material contained in the ink may have some evidential value. For example, the fine asbestos fibres found in a letter written in 1930 from an engineer's office (Pl. II, 20) is suggestive of the origin of the letter. In another instance plant débris (probably straw dust, for it gave a ligno-cellulose reaction) was found in a letter of June, 1917, whilst similar particles were found in another letter written from the same house, but a month later (Pl. II, 14 and 15).

In a legal document a letter had been added to certain words, either by the original writer immediately after the writing was completed or fraudulently by another person on a subsequent date. Since it was not permissible to bleach the ink-strokes, which were in a heavy record ink and had not been blotted, search was made throughout the writing for thin portions in which sediment might be visible under the microscope. At seven points some sediment was detected. The added letters had been blotted, and the sediment also was easily visible. From the character and distribution of the various sediments it was highly probable that the added letters were written with ink from the same pot as used for the earlier writing. This conclusion was subsequently confirmed by other evidence.

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* The principle adopted was that of the "gravitv column," originally described by Sollas, in which a column of mixed liquids gradually increasing in density downwards is used. A narrow glass tube, about 80 cm. in length, was filled with a mixture of benzene and pure bromoform (commercial samples are frequently impure), the proportion of the latter increasing towards the bottom of the tube, thus giving a column of liquid ranging in sp.gr. from about 0·88 at the top to 2·90 at the lower end. The fragment of unknown material was dropped into the tube, and small glass bulbs or small (insoluble) crystals of inorganic salts of known sp.gr. were then added until one remained slightly above the fragment, and one just below it; the desired value was hen obtained by calculation.

DISTRIBUTION OF SEDIMENT IN WRITING.—The sediment transferred by the pen from the ink-pot to the paper may afford an indication of the stages in the course of the writing at which the pen was dipped into the ink. The strokes produced immediately after dipping sometimes contain the greater proportion of a heavy sediment, which diminishes (rapidly or slowly) in amount as the writing proceeds. Conversely, a light floating sediment, such as mould spores or insect débris, will occasionally increase in amount as the pen becomes depleted of ink.

METHODS FOR THE EXAMINATION OF DEPOSITS IN WRITING

For most specimens of writing a microscopical examination without any preliminary preparation is satisfactory. The writing may be examined as an opaque object by reflected light, by transmitted light if on translucent paper, or by a combination of the two methods. Owing to reflection from the glossy, and sometimes fluorescent, surface of many ink-strokes the modern methods of vertical illumination are seldom of value in the examination of ink sediments.

In some writings the normal ink-colour is in large amount, and almost obscures any sediment beneath. To overcome this absence of contrast and differentiate the sediment, the stroke may be partly bleached by spotting with $N/10$ hydrochloric acid, the excess of which is removed with filter-paper after a few seconds, and this treatment is repeated, if necessary. By this procedure the normal ink-colour is considerably lightened in tint, whilst the sediment is apparently unaffected, and may be readily observed and photographed.

IDENTIFICATION OF THE SEDIMENT OR DEPOSIT.—Sometimes the microscopic appearance of the sediment is in itself sufficient to enable one to determine its character, especially with organised structures such as plant and insect débris, textile fibres, etc. Other materials, however, may have to be removed from the writing, and the microscopic fragments submitted to a physical and chemical examination before their identity can be established. Of the various methods tried, we have found the following the most successful:

(*a*) *Sediments Soluble in Water.*—The ink-stroke is moistened with a minute drop of benzene, and gentle manipulation with a short, rigid, mounted needle will isolate the fragment, which is then dried and examined. The use of a rigid needle is emphasised, since a flexible one leads to much loss.

(*b*) *Sediments Relatively Insoluble in Water or Dilute Acid.*—The writing is brushed lightly with water or $N/10$ hydrochloric acid, and the fragments are collected in a camel-hair brush, which is then rinsed into water contained in a small centrifuge tube closed at the lower end with a rubber stopper. After being centrifuged the supernatant liquid is gently syphoned off, and, if necessary, the residue is washed with dilute hydrochloric acid and water in the tube to eliminate ink-colour. After the wash-water has been removed, the rubber stopper, bearing the residue on its end, is withdrawn. The separated particles are dried at a low temperature, and the specific gravity of one fragment is determined by means of a gravity column of mercuric iodide in potassium iodide solution, or of bromoform and benzene (*vide supra*). This is followed by microscopical examination to determine the crystallographic system, refractive index and angle of extinction in polarised light, after which suitable microchemical tests may be made. We have found it possible in some cases to identify a quantity of sediment not exceeding 0·05 mgrm. in weight.

PHOTOMICROGRAPHIC PROCEDURE.—Most of the photographs shown in the figures are magnified 50 diameters, this being obtained with an objective of 75 mm. focal length, and an eyepiece giving a magnification of 8 diameters. The specimens were illuminated as opaque objects with a bull's-eye condenser, and in some instances a little transmitted light was also used.

For documents from which small portions may be removed, illumination by means of the old-fashioned Lieberkühn reflector yields satisfactory results, and it has the advantages over vertical illuminators of being simpler to manipulate and of giving slightly angular illumination, which tends to eliminate confusing reflections from the surface of the ink.

Many colour filters were tried in order to reduce or eliminate the ink-colour and render the dark sediments prominent, and a diluted blue-black ink was found to yield good results in many cases. (*Cf.* Ward, ANALYST, 1930, 55, 568.) The most generally useful filter for this purpose, however, was prepared by dissolving the ferric tannin compound (precipitated on keeping an ink without added dye for a long time) in fused phenol, and diluting the solution with water. With this filter the definition obtained is not particularly good, owing partly to the difficulty of focussing with the faint blue light available, and partly to the filter allowing some red light (in addition to blue and violet) to pass. To secure contrast when photographing extraneous deposits on the surface of the ink-strokes, a filter composed of a 10 mm. layer of a 0·35 per cent. aqueous solution of tartrazine was employed.

Most of the photomicrographs were taken on Wellington Anti-Screen plates, but, where the writing had become brownish in colour, Ilford Soft Gradation Panchromatic plates were used.

We wish to thank Mr. S. Creasey for his assistance in the analytical work.

DESCRIPTION OF THE PLATES

PLATE I

FIG.

1. Pen stroke with ink containing normal sediment × 50.
2. Pen stroke with ink containing excess of tannin × 50.
3. Excess of iron × 50.
4. Excess of gallic acid × 50.
5. Stroke made in ink, partly thawed × 50.
6. Effect of pen left in ink × 50.
7. Mould hyphae in ink-writing × 50.
8. Effect of alkaline glass on ink × 50.
9. Writing in ink containing oxalic acid in the sediment × 100.
10. Sand on writing in letter, 1842 × 50.
11. Sand on writing in book, 1840 × 50.
12. Pumice granules on writing in letter, 1837 × 100.

PLATE II

FIG.
13. Brown sand on writing in letter, Cairo, 1932 × 50.
14. Plant débris in ink-writing in letter, June, 1917 × 100.
15. Plant débris in ink-writing in letter, from the same house, July, 1917 × 100.
16. Plant hair in writing in letter, 1902 × 100.
17. Moth scales in writing in letter, 1894 × 50.
18. Moth scales (experimental) in ink-writing × 50.
19. Potato starch in ink-writing in letter, 1904 × 50.
20. Asbestos in ink-writing in letter from an engineer's house, 1930 × 100.
21. Calcium sulphate in ink-writing in laboratory notebook, 1896 × 25.
22. Effect of chalk in the ink × 50.
23. Sediment in ink in laboratory notebook, 1896 × 25.
24. Blotting-paper fibres on ink in letter from Paris, 1932 × 50.

DISCUSSION

The **PRESIDENT**, after commenting on the careful and remarkable manner in which this research had been presented, said that his own connection with ink was in rather a different category. He occasionally had to give an opinion as to the amount of sediment that an ink would give when in use, and he suggested that it might be possible to devise a method for determining this. He could very strongly support, as a good test for acid, the immersion of two or three clean, weighed nibs in the ink two or three days, and then wiping and re-weighing them. One could get very sound information, and, further, one was treating the actual material to be used in the ink. He had not realised, until Dr. Mitchell had mentioned the fact, that the subsequent addition to the American report was derived from Dr. Mitchell's suggestion.

Mr. R. F. **INNES** said that he was exceedingly interested in the paper, but from a different point of view than the authors had in mind. Could the authors say whether the oxidase in the mycelium of certain moulds would be able to act in the absence of iron. Presumably in the nib test the nib must be a steel nib. Was there any correlation between the corrosive action and the p_H of the ink?

Mr. E. R. **BOLTON** asked whether sodium fluoride had been tried to prevent the growth of moulds.

Mr. A. **SCIVER** expressed his appreciation of this very interesting paper. He, too, had been working on writing-inks for five or six months, and, although he did not wish to appear too much of an iconoclast, he had come to the conclusion that there was no really good ink on the British or American markets.

He asked whether the strokes in the first six slides were made with a brush or with a pen. With regard to the freezing of ink, he had recently been informed by a Japanese firm that the ink to be used by Russian and Japanese armies in Siberia had to resist intense cold, and that it would often freeze solid in the officers' fountain pens. Hence there must be some inks not affected by freezing. He, too, had intended to suggest the use of sodium fluoride as a preservative, but there were a number of efficient organic compounds available to-day.

With regard to the nib-corrosion test, he had found that practically all inks would produce a semi-solid crust if steel nibs were left in them. In his experience, the test had not proved successful, for, apart from the solution of the steel, he found it difficult to know when to stop rubbing the encrusted material from the nib after immersion in the ink. He asked whether any published figures were available of the p_H of inks now on the market. He had been unable to trace any direct connection between the p_H of an ink and the formation of sediment. It was difficult to devise a method that would give an indication of the weight of a sediment, but a simple volumetric method could be used. Had the authors tried the method of measuring the sediment in a long piece of tubing drawn out to a fine bore at one end?

In his opinion the development of sediment in ink required to be examined from the aspect of physical chemistry, and in particular from the aspect of colloid chemistry, as distinct from the ratio of the tannin and iron.

Dr. J. GRANT mentioned that papers of good quality were passed through a bath of very strong gelatin solution, and he wondered if this might affect the sediment in the ink used on the paper.

Mr. WARD, replying, said that in devising a standard method for determining the time of sedimentation it was necessary to take into consideration whether the ink was kept in a closed or an open bottle. If open, there were numerous factors which might influence the sedimentation.

With regard to the use of oxidation by moulds for the estimation of oxydase activity, it was quite possible that the presence of iron was not essential. Some two years ago Guthrie (ANALYST, 1930, **55**, 709) had estimated oxydase action by using the substrate formed by heating glucose with sodium hydroxide. The nib for the corrosion test should certainly be of steel, and not of stainless steel or gold. Different inks were stabilised with different acids—some with sulphuric, others with oxalic, and others, again, with acetic acid, and the degree of corrosion would vary with the acid. He had always found that brushing the nib with a tooth-brush in water was a satisfactory method of removing the incrustation.

Referring to the solidification of ink, Mr. Ward mentioned that he had seen an ink 75 per cent. of which became a solid jelly. It was contained in a cheap German fast-filling container of soda-glass. One had only to add a drop of water to the glass to obtain a distinctly alkaline solution.

The photomicrographs of the earlier slides all represented strokes made with a pen in the usual way. Referring to the photomicrograph showing the deposit of potato-starch in the writing, he mentioned that this deposit could be seen all through the letter, and was therefore obviously in the ink.

He did not agree with the observation of Mr. Sciver, that there was not a really good ink on the market; it depended upon the connotation of "really good." If one could buy an ink which would keep in good condition in the bottle for at least six months, he would consider that a satisfactory ink.

Dr. MITCHELL said that no definite relationship had been established between the p_H value and the corrosive action of different inks, although the determination of the hydrogen ion concentration was of comparative value. On the other hand, the method which he had devised of adding sodium acetate to an ink and distilling the liberated acetic acid (ANALYST, 1921, **46**, 131) had been found to afford a measure of the corrosive acid and acid compounds in an ink. Sodium fluoride would be an effective preservative against moulds, but would have the drawback of attacking the glass of the bottle. His remarks about the freezing of ink had been misunderstood: he had meant that it was unreasonable to complain of the results obtained with a half-thawed ink. A good ink should recover its original composition and properties after thawing. Physical methods of determining the stability of inks would probably prove of value, but in his experience the ratio of tannin to iron was as yet the best criterion. It was possible, as Dr. Grant had suggested, that the sizing material of the paper might affect the constituents of some inks. Mr. Sciver's volumetric method of measuring the sediment might sometimes be useful, but with many inks it would be difficult to determine the line of demarcation, owing to the dark colour of both ink and deposit.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE ACIDITY OF GORGONZOLA AND STILTON CHEESES

In 1922 some Stilton cheese came under notice because of a complaint of "a burning taste." The article had an acidity of 1·94 per cent., calculated as lactic acid.

In 1929 there was a further complaint, this time of a Gorgonzola cheese, alleged to have "a chemical taste," and it certainly had a sweetish acid taste, but not an unusual one for this type of article. It contained 1·60 per cent. of acid, calculated as lactic acid. Copper was present to the extent of one-fifteenth grain per pound.

As no other objectionable substance was found in either cheese, it seemed reasonable to attribute the taste in each instance to excess of lactic acid, provoking reactions in the tissues of mouths that may have been hyper-sensitive or sore through either inflammation or wounds, or because of food or drink taken previously.

Analyses of other samples of Gorgonzola cheese and one of Stilton (the twelfth in the table that follows), none of which appeared to be the subject of complaint, showed that, whilst amounts of 1·94 and 1·60 per cent. of lactic acid are above the average, they are not exceptional. But they do seem to indicate the zone of 1·6 to 1·9 per cent. of lactic acid to be that where occasional complaints may be expected, especially in articles in which the public has been educated by writers in popular weekly journals to expect copper salts.

The method for determination of acidity used was that given by Leach in *Food Inspection and Analysis*, Second Edition, 1909, p. 207, who cites as the source: *U.S. Dept. of Agric., Bureau of Chem. Bul.*, 46, p. 56. Reference to the latter shows the original source to be "Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (U.S.A.)" of 1898.

Few references to the subject are to be found in chemical literature, but John Muter (ANALYST, 1885, **10**, 6) gives the average amount of water for Stilton cheese as 28·60 per cent., and the average acidity as 1·08. James Bell (*Chemistry of Foods*, 1883) gives for Stilton 23·57 per cent. of water and 1·24 per cent. of free acid (as lactic). Bell also gives figures for Gorgonzola cheese as 31·85 per cent. of water and 1·35 per cent. of free acid as lactic acid.

The data are arranged in order of the lactic acid content:

Number	Water Per Cent.	Acidity, as lactic acid Per Cent.	Number	Water Per Cent.	Acidity, as lactic acid Per Cent.
1	28·1	0·36	11	35·5	1·12
2	34·6	0·54	12	32·9	1·22
3	—	0·55	13	32·0	1·29
4	35·6	0·73	14	44·9	1·42
5	36·1	0·77	15	32·3	1·44
6	44·3	0·85	16	42·5	1·48
7	28·8	0·89	17	37·5	1·60
8	29·3	0·90	18	38·5	1·72
9	38·2	0·91	19	27·9	1·84
10	31·7	1·05	20	27·5	2·14

Comparison of the figures for water-content and acidity seems to show that there is no relation between them.

Three of the samples (Nos. 9, 16, and 6) contained fat in amounts (20·8, 28·0, and 28·9 per cent., respectively) substantially below that usual for Gorgonzola cheese.

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THE EXTRACTIVES OF RUM

IN *Aids to the Analysis of Food and Drugs*, Fourth Edition, 1918, there occurs the statement (p. 186) that rum contains from 0·7 to 1·5 per cent. of total solids. This being a datum that can be altered at the discretion of the manufacturer to suit the palates of purchasers, the matter is not of great importance, but the limits given were those stated by Pearmain and Moor in 1899, and do not appear to be characteristic. *Suggested Standards of Purity for Foods and Drugs* gives even higher figures in stating that "The extractive usually varies from 1·0 to 2·0 per cent." Church in *Food* (1882), p. 181, described a genuine sample of rum from the West Indies as containing "36½ grains of solid residue per pint." This corresponds with 0·42 per cent. w/v. Further, A. W. and M. W. Blyth, in *Foods : Their Composition and Analysis*, Sixth Edition (1909), p. 399, say: "As imported rum is a strong spirit containing 44 to 55 per cent. absolute alcohol, and from 0·3 per cent. to 1·0 per cent. extract, retailers mostly dilute it down nearer the legal limit of alcoholic strength."

The figures for the extracts given by forty-three samples of rum from various sources are tabulated below. The minimum was 0·30 and the maximum 1·13 grm. of total solids per 100 c.c. This shows fair agreement with the limits given by A. W. and M. W. Blyth. (Thirty-six of the samples were of the 30 U.P. type.)

Extract per 100 c.c. Grms.	Number of samples
0·30 to 0·40	11
0·41 to 0·50	7
0·51 to 0·60	6
0·61 to 0·70	7
0·71 to 0·80	6
0·81 to 0·90	4
0·91 to 1·00	0
1·01 to 1·10	0
1·11 to 1·13	2
Total number of samples examined	43

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THE BRITISH PHARMACOPOEIA ANTIMONY TRICHLORIDE COLOUR TEST FOR COD-LIVER OIL

IT is apparent that there is considerable doubt among chemists as to how to recognise the colour specified in the British Pharmacopoeia, 1932, in the test for cod-liver oil by the antimony trichloride reaction.

The limit recommended in this test corresponds with the colour of the Lovibond blue glass, No. 6·0.

THE COLOUR LABORATORY, MILFORD, SALISBURY

THE TINTOMETER, LTD.

THE DETERMINATION OF META- AND ORTHO-CRESOLS

SINCE the publication of our method for the determination of meta- and ortho-cresols in THE ANALYST (1932, p. 567) we have found that the precipitation of the aldehyde resins is best effected by cooling the liquid to 50° C. before adding the hydrochloric acid, and by subsequent dilution with a further 25 c.c. of water.

This always yields a fine precipitate, free from other compounds which might become occluded if the separated solid is aggregated in lumps, and it may be readily washed clean and dried to constant weight at 100° C. before filtration.

We have received evidence that other workers can obtain concordant results, provided the resin is precipitated in a finely-divided condition, and this is ensured by following the modified procedure outlined above.

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Report of the Essential Oil Sub-Committee to the Standing Committee on Uniformity of Analytical Methods

ESSENTIAL OILS. REPORT No. 10

THE DETERMINATION OF CITRONELLAL

THE Essential Oil Sub-Committee recommends the following modification of the hydroxylamine method for the determination of citronellal. This has been found to give excellent results in practice, but certain precautions are necessary as the reaction between citronellal and hydroxylamine hydrochloride takes place rapidly in the cold in a slightly acid solution, but very slowly in alkaline solution. In addition citronellal is rapidly destroyed by free hydrochloric acid, so that it becomes important to neutralise, as quickly as possible, the free acid liberated in the reaction. At the same time the reaction mixture must not be allowed to become alkaline. The following solutions are required:

Indicator Solution.—A 0·2 per cent. solution of dimethyl-yellow (*p*-dimethylaminoazobenzene) in 90 per cent. alcohol.

N/2 Alcoholic Potash.—Prepared with 90 per cent. (by volume) alcohol and standardised against *N*/2 hydrochloric acid, using dimethyl yellow as indicator and running the alkali into the acid until the full yellow colour is obtained.

N/1 Hydroxylamine Hydrochloride Reagent.—Dissolve 6·95 grms. of pure hydroxylamine hydrochloride in 95 c.c. of 90 per cent. (by volume) alcohol, add 0·4 c.c. of dimethyl yellow solution, adjust to the full yellow colour of the indicator with *N*/2 alcoholic potash, and make up to 100 c.c. with 90 per cent. (by volume) alcohol.

The alcohol used must be free from aldehydes and ketones.

The full yellow colour of the indicator may be defined as that colour which is not changed by the further addition of alkali. The correct adjustment of the reagent should be confirmed in the following manner:

Place 10 c.c. in each of two tubes, and to one tube add 1 drop of *N*/2 alcoholic potash; no change in colour should be observed. To the other tube add 1 drop of *N*/2 hydrochloric acid; a slight change in colour towards orange should be produced.

METHOD OF DETERMINATION.—Into a stoppered tube approximately 150 mm. long by 25 mm. diameter, weigh accurately such a quantity of the oil as contains about 0·8 grm. of citronellal and cool to a temperature of 0° (or lower). Add about 10 c.c. of the *N*/1 hydroxylamine hydrochloride reagent previously cooled to 0°, and titrate the liberated acid *immediately* with *N*/2 alcoholic potash, adding the alkali very cautiously and *taking great care to avoid going beyond the orange colour of the indicator.* Continue the titration as long as the red colour develops, then allow the mixture to stand at laboratory temperature for 1 hour and complete the titration to the full yellow colour of the indicator.

The number of c.c. of *N*/2 alcoholic potash required, multiplied by the correcting factor 1·008, by the factor 0·077 for citronellal, and by 100, and divided by the weight of oil taken, will give the percentage (by weight) of the aldehydes, calculated as citronellal.

The correcting factor is necessary owing to the fact that the end-point of the titration occurs at a p_H different from that of normal hydroxylamine hydrochloride.

The results of determinations of citronellal in a sample of Java citronella oil circulated to the members of the Sub-Committee are given in the following table. We are of opinion that the maximum variation in the percentage of citronellal, as determined by this method, should not exceed ±0·5 per cent.

PERCENTAGE OF CITRONELLAL IN JAVA CITRONELLA OIL

Sub-Committee Member		Sub-Committee Member	
1.	33·0	6.	33·1
	33·3		33·1
2.	32·8		33·2
	32·9		33·3
3.	33·2	7.	33·5
4.	33·4		33·7
	33·4		33·8
	33·2	8.	33·2
5.	33·1		33·8
	33·4	9.	32·9
			33·1

Variation	32·8 to 33·8
Mean	33·26

(*Signed*),

John Allan (Chairman), C. T. Bennett, S. W. Bradley, E. Theodore Brewis, L. E. Campbell, Thos. H. Durrans, T. W. Harrison, Ernest J. Parry, C. Edward Sage, W. H. Simmons, T. Tusting Cocking (Hon. Sec.).

21*st September*, 1932

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(From the beginning of the year 1921 to date)

II LEAD

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Zellner. Lead in Sardines in Oil. *Deut. Nahrungsm. Rundschau*, 1929, **4**, 23; *C.A.*, 1929, 3520. (Fifty per cent. of samples examined contained lead.)

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

Annual Report of the City Analyst for 1931

Of the 6009 samples submitted for analysis, 5003 were taken in connection with the Sale of Food and Drugs Act, and included 2617 milks (238 incorrect), 446 butters (2 incorrect), 258 margarines (1 incorrect), and 106 lards (all genuine). The total percentage returned as incorrect was 6·3.

"Extra Cream Ice."—Twelve samples of ice cream and cream ice contained butter-fat in amounts varying from 2 to 24 per cent. In the absence of any legal standard for ice cream, all the samples but one were passed as genuine. This was described on the label as "Extra Cream Ice," which would lead the purchaser to suppose he was getting an article superior to ordinary cream ice, which itself should contain more fat than ice cream. The sample contained only 2 per cent. of fat, which was the smallest amount found in any of the samples. It was returned as being falsely labelled.

Chalk in Sweets.—Samples of sweets, in the form of tablets, contained a core of flavoured chocolate covered with a film of gum, followed by a layer of French chalk and chalk, the whole being covered with coloured sugar. The total extraneous mineral matter was over 10 per cent., and the manufacturers were asked for an explanation. Among other reasons for the inclusion of the chalk, it was claimed that it would help to make good the deficiency in calcium in the ordinary diet, and so would be beneficial rather than harmful. Finally, however, they agreed to manufacture the tablets in such a way as to avoid the use of chalk or other insoluble matter.

"FRUIT DRINKS."—Analysis of three samples of mineral waters, described as "Fruit Drinks," showed that they contained no genuine fruit juice, the ingredients being citric acid, the essential oil of the fruit mentioned on the label, and sugar. The makers agreed to withdraw the term "Fruit Drink."

H. H. BAGNALL

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

TRADE DESCRIPTION OF WINES

ON October 31st a firm of British wine manufacturers was summoned at Clerkenwell Police Court for selling, contrary to the Merchandise Marks Act, 1887, certain bottles of liquor to which a false trade description (*e.g.* sauterne, burgundy, chablis, vermouth) had been applied.

Mr. Monier-Williams, for the prosecution, contended that the contents of the bottles were quite different from the genuine products connoted by the respective names, and that the labels were calculated to lead the purchaser to think that he was getting the genuine wines.

The defence was that the liquors were produced from musts from grapes grown in Sardinia.

The Magistrate (Mr. Pope), in giving judgment, said that these wines were made from imported musts, and he had been asked to say that such names as "burgundy" had become generic terms and were no longer confined to the products of the Continental countries from which they had originated. There might be strong reasons for getting that view promulgated under competent authority, but the governing idea of the Statute was the idea created in the mind of the public.

He held that the use of the words "sauterne," "burgundy," etc., was fundamentally untrue, even with the addition of the letters "P.M.P." (meaning Pure Must Product), which the public would not understand. Why make such free use of French names if there was no intention to mislead? Referring to the "French vermouth," the Magistrate said that, as the word "type" had been added, it would not be fair to convict in that case, but the "Italian vermouth" was presented in such a way as to amount to a false trade description.

He imposed a fine of 40s. in each of the seven cases, with five guineas costs on each summons.

Cyprus

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1931

THE Government Analyst (Dr. J. G. Willimott) states that 1749 samples were examined, of which 778 were food and drugs and 449 were in connection with criminal cases. Of the 88 samples of food and drugs found to be adulterated, 58 were of coffee and 14 of milk. Some form of starch was used for the adulteration of the coffee, and the milk was either skimmed or watered. It appears that lye water, prepared from wood ashes, is frequently used as an adulterant of milk, the idea being that the specific gravity is not thereby affected.

LABELLING OF FOOD AS "ADULTERATED."—Many shopkeepers, presumably on legal advice, have adopted the sharp practice of labelling every foodstuff as "adulterated," in the belief that by so doing the vendor renders himself immune from prosecution. From certain decisions given in the Courts it would appear that practices of this nature are legally permissible.

CASES OF ANIMAL POISONING.—Five of twenty viscera taken from the different farm animals of Cyprus were found to contain white arsenic. A certain amount of the arsenic used in the past for the destruction of locusts is still in the hands of the villagers, and is thus easily available when any poisoning is to be done.

QUININE POISONING.—A fatal case of quinine poisoning occurred at Amiandos, where a girl, five years old, swallowed 25 five-grain tablets of sugar-coated quinine tablets in the belief that they were sweets. Vomiting and purging soon came on, followed by cyanosis, collapse, and death within three hours. Quinine was found in the stomach and traces in the liver. Particulars of the *post-mortem* examination were published in the *Lancet* of November 21st, 1931.

PIGMENTS OF THE POLLEN OF CERTAIN LILIES.—The pollen and anthers of certain lilies yield, on suitable extraction, a pigment which can act as a sensitive indicator with acid and alkali. The colour in dilute acids is a pink-red and in dilute alkalis a bright green, the end-point being remarkably sharp. In titration work these indicators were found to give the same results as methyl red or litmus. The best method of extraction is one of simple maceration of the anthers at room temperature. When extraction of the indicator pigment is attempted in 90 per cent. alcohol, several other pigments are extracted at the same time, thus giving a heterogenous solution. The confusing pigments consist of a considerable amount of carotene, a little xanthophyll and another unknown pigment. The indicator pigment is also present in the flowers, from which it was isolated and proved to be an anthocyanin.

Fiji

REPORT OF THE GOVERNMENT CHEMIST FOR THE YEAR 1931

IN his annual report to the Department of Agriculture, Fiji, Mr. J. W. Blackie states that 717 samples were analysed as against 541 in 1930. These included 130 of milk, 51 of other foods, 27 of drugs, and 17 of aerated waters.

MILK.—As a result of the rigid inspection of dairies the milk has been much cleaner than in former years. It has been argued in the past that it is impossible to produce milk in Fiji up to the standard required by law in England, namely, 3·0 per cent. of fat, 8·5 per cent. of solids-not-fat. This feeling has resulted from the consistently poor quality of the milk offered for sale. The figures obtained during this year, which has not been exceptional, show definitely that milk can be produced in Suva of a quality equal to that in temperate countries, and, provided that the herds are healthy, there is no reason why a standard of 3·2 per cent. of fat and 8·5 per cent. of solids-not-fat should not be enforced, instead of the low requirement of the dairy by-laws now in force, namely, 3·0 per cent. of fat and 8 per cent. of solids-not-fat.

The research work carried out during the year included the following investigations:

DIDI RESIN.—The resinous substance exuding from *Canarium vitiensi* is used locally as an adulterant of kauri resin. It was found to contain 26·5 per cent. of a resene (m.pt. 183° to 185° C.), soluble in ether and in chloroform; 53 per cent.

of other resenes, soluble in alcohol; and 5·8 per cent. of an essential oil. The alcohol-soluble portion would have some value as a lacquer for metals.

TOXIC PRINCIPLE OF LANTANA CROCEA.—A strange cattle disease, attributed to ingestion of *Lantana crocea*, was investigated. The veterinary evidence indicated that substances akin to lupino-toxins were present, but, up to the present, these have not been detected. A trace of an alkaloidal substance was isolated, and is under investigation. Feeding experiments and injections with extracts of the plants under examination failed to produce the characteristic lantana symptoms, but, as the veterinary officers obtained positive results with other specimens, it is suggested that there may be seasonal variation in the active principle.

ETHYL ESTERS OF CALOPHYLLUM (DILO) OIL.—The "ethyl esters" of dilo oil, obtained from the kernels of *Calophyllum inophyllum*, were found to consist of about 50 per cent. of unesterified material containing the glycerides of oleic, palmitic and stearic acids, together with resin acids and resenes. The esterified portion contained about 20·6 per cent. of ethyl oleate and 79·4 per cent. of ethyl palmitate and ethyl stearate in approximately equal proportions. The natives use the oil for massaging purposes, and some success has attended the use of the ethyl esters for the treatment of leprosy.

ROTENONE-CONTENT OF DERRIS ULIGINOSA.—The local species of *Derris*, termed *duva* by the natives, has some reputation as a stupefying agent for fish, but, in general, the imported species, *Derris elliptica*, is used. Comparative analyses of the two species showed that the "derrid" content (*i.e.* ethereal extract) of the latter is at least six times as much (*e.g.* 12·0 and 1·8 per cent.). For the determination of the rotenone content the apparatus previously described (*J. Soc. Chem. Ind.*, 1932, 51, 129T) was used for extracting the material. The following results were obtained with a composite sample of stem and root:—Moisture, 12·2; rotenone on air-dried substance, 0·3; on dry substance, 0·34 per cent. Derris root has been reported to contain as little as a few tenths of a per cent. of rotenone, but the best commercial samples contain from 4 to 5 per cent.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Rapid Method for the Determination of Moisture in Flour and other Finely-divided Materials. E. A. Fisher and J. Thomlinson. (*J. Soc. Chem. Ind.*, 1932, 51, 355–358T.)—In a patented apparatus (B.P. 365,247), a known weight of the flour is mixed with finely-powdered calcium carbide, the loss in weight of the charged apparatus representing acetylene, from which the moisture reacting with the carbide may be calculated. The method requires calibrating by means of determinations made by the ordinary drying-oven method, as it gives low results, owing to the fact that part of the moisture does not react with the carbide and for other reasons. For the percentage of moisture in a single sample of flour, sixteen pairs of determinations gave results varying from 14·34 to 14·74 by the drying method, and from 13·02 to 13·28 by the method described. The differences between the results obtained simultaneously by the two methods ranged from 1·18 to 1·65, and had the average value 1·36. When the results given by the new method were increased by this average correction, the drying method yielded figures varying from 0·20 below to 0·29 above those of the carbide method. For about 30 commercial flours the two methods gave results differing by 1·20 to 1·90, the average difference being 1·48.

If the loss in weight of the apparatus is determined after the reaction has proceeded for 20 minutes—by which time the system has become reasonably cool—further reaction is comparatively slight with flours containing over 10 per cent. of moisture, but proceeds to an appreciable extent and during a protracted period with flours containing less than 8 or 9 per cent. T. H. P.

Sulphur Content of Foods. K. S. Kemmerer and P. W. Boutwell. (*Ind. Eng. Chem., Anal. Edit.*, 1932, 4, 423–425.)—A quantity of the sample sufficient to contain from 3 to 5 mgrms. of sulphur is digested with nitric acid, and the excess of the acid is evaporated; 10 c.c. of 70 per cent. perchloric acid are then added, and the mixture is boiled until the volume is reduced to about 1 c.c. The excess of perchloric and nitric acids is removed by evaporation with the addition of hydrochloric acid, the residual solution is neutralised with ammonia, boiled, rendered slightly acid with hydrochloric acid, and filtered, and the filtrate is treated with ammonia, then just acidified with hydrochloric acid, litmus being used as indicator, and diluted to a definite volume. The sulphuric acid is then determined, as barium sulphate, in a turbidimeter. A modified Burgess–Parr turbidimeter for the purpose is described. Results of the determination of sulphur in a large number of foods are given, and the following are selected as typical examples:—Apple, 0·018; asparagus, 0·065; red beet, 0·017; white bread, 0·011; whole-meal bread, 0·104; carrots, 0·016; celery, 0·025; cocoa, 0·236; coffee beans, 0·131; garlic, 0·506; lettuce, 0·016; ham, 0·130; beefsteak, 0·202; whole milk, 0·028; mustard seed, 1·175; oatmeal, 0·233; potatoes, 0·049; pepper, 0·035; spinach, 0·030; tea, 0·217; wheat flour (40 per cent. gluten), 0·470 per cent. All the percentages are calculated on the wet substance or on the material as offered for sale.
W. P. S.

Precipitation of Sugars and Polyhydric Alcohols by Metallic Hydroxides in Alkaline Media. I. General Character of the Precipitation. P. Fleury and J. Courtois. (*J. Pharm. Chim.*, 1932, 16, 97–109.)—Precipitation of sugars and polyhydric alcohols (glycol, erythritol, mannitol, etc.) from solutions containing a heavy metal salt on addition of an alkali hydroxide appears to be a general reaction. The precipitation is more nearly complete (1) with barium hydroxide than with either ammonium or sodium hydroxide, (2) with iron than with any other of the heavy metals tried, and (3) with acetates of the heavy metals than with nitrates. T. H. P.

Additional Tests in Honey Analysis. J. Grüss. (*Z. Unters. Lebensm.*, 1932, 64, 376–383.)—It is considered that the best honeys should show all the enzymic reactions of the living plant-cell. (1) As a test for oxidase action, 1 grm. of honey is mixed with 5 c.c. of a freshly-prepared solution containing 0·5 to 1 mgrm. of violamine, 5 c.c. of the reagent without honey being placed in a similar vessel as a control. After 2 hours an upper violet and a lower colourless zone should appear in the vessels containing the sample, whilst the control is deep violet throughout. The zones given by different types of honey differ to a pronounced extent in the depth of the coloured zone. For a quantitative determination the mixture is transferred to a flask, and the colourless liquid is titrated with sodium bisulphite solution, or preferably, with a 0·1 *N* solution of sodium thiosulphate in the presence of acetic acid; the values obtained with fruit-, lime-, heather- and robinia-honey were 0·4, 1·0, 1·2, and 1·8 c.c., respectively. The higher the oxidase value the better the honey. (2) The hydrogenase activity is measured by the action of a 10 per cent. solution of honey on an equal weight of milk of sulphur, and the hydrogen sulphide evolved after 2 days at 25 to 28° C. is assessed from the intensity of the stain on a lead acetate paper, or it may be determined exactly by leading it into a solution of a cadmium salt, and weighing the resulting sulphide. (3) One of the usual iodine-starch reactions is used for the evaluation of diastase. The four above-mentioned samples of honey were shown to contain (per grm.) 9005, 1560, 5473, and 1891 grains of pollen, 30, 120, 95, and 335 mould colonies, numerous cocci, and a number of yeast cells. A new yeast (*Anthomyces ruber, n. sp.*) was observed in lime honey and a new *Mucor* mould (*Cephalosporium candidum, n. sp.*) in heather honey. The moulds (which included *Dematia, Penicillia* and *Mucor* types) were usually responsible for the reducing action towards sulphur. J. G.

Specific Test for Orange Honey. R. E. Lothrop. (*Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 395–396.)—Californian orange honey owes its characteristic flavour and aroma to the presence of methyl anthranilate. This substance is not present in honey obtained by bees from other sources. To detect methyl anthranilate 1 kilo. of the honey is dissolved in 800 c.c. of water and steam-distilled; 700 c.c. of distillate are collected and extracted with chloroform, the extract is evaporated in a current of air until the chloroform is just removed, and the residue is dissolved in 2 c.c. of 10 per cent. sulphuric acid. The solution is treated with one drop of 5 per cent. sodium nitrite solution, a few crystals of urea are added to remove excess of nitrous acid, and the solution is added to a mixture of 1 c.c. of 0·5 per cent. β-naphthol solution (in dilute sodium hydroxide solution), 1 c.c. of 10 per cent. sodium hydroxide solution, and 1 c.c. of 10 per cent. sodium carbonate solution. A yellowish-red precipitate is produced if as little as 0·1 mgrm. of methyl anthranilate is present. W. P. S.

Detection and Determination of a Proprietary Oil (Sonderöl) [added to Edible Fats]. H. Schmalfuss and H. Werner. (*Z. Unters. Lebensm.*, 1932, 64, 362–367.)—The oil, which, according to Schou (E.P. 187,298, 16.11.22), is added to edible fats, is brown in colour, viscous, sparingly soluble in ethyl and propyl alcohols and in petroleum spirit, and readily soluble in all other common organic solvents. Analysis gave: n_D^{40}, 1·467; saponification value, 205; Reichert-Meissl value, 7·5; Polenske value, 8·7; iodine value (Hanus), 51; hydroxyl value, 24·0; acetyl value (Elsbach), 23·0; acid value, 3·0. As a qualitative test 15 c.c. of petroleum spirit (b.pt. 30° to 50° C.) are shaken with 1 grm. of sample in a stoppered tube, when 1 per cent. or more of the oil produces a white opalescence coagulating to a yellow or brown deposit; neither hardened nor blown whale oil react. For quantitative work the insoluble matter from 2 to 30 grms. of sample is removed by filtration, then washed 4 times with petroleum spirit and dried in nitrogen at a low temperature, and weighed. A curve shows the correction for the solubility of the precipitate in the mixture of fat and petroleum spirit. The precipitate contains no sulphur, nitrogen or mineral matter, and all except 0·2 per cent. is saponifiable, the acid precipitated from the resulting soap being partly soluble in petroleum spirit, and partly volatile, and having a mean molecular weight of 256. J. G.

Composition of Kapok Seed Oil. R. C. Malhotra. (*J. Indian Chem. Soc.*, 1932, **9**, 413.)—Analyses of the oils of *Eriodendron anfractuosum* seeds from Java, Sumatra, and Malaya show wide variations in the composition, which appears to be modified by the time of collection of seeds, methods of storage, age and variety of the parent plant and nature of the soil, as well as by the geographical position.

	Java	Sumatra	Malaya
Sp.gr. at 25° C.	0·9105	0·9216	0·9387
Saponification value ..	170·8	179·2	198·1
Iodine value (Hanus) ..	96·3	95·7	91·3
Saturated acids, per cent...	18·90	17·35	19·60
Unsaturated acids, per cent.	75·98	76·56	75·00

D. G. H.

Castor Oil 135 Years Old. N. Evers. (*Pharm. J.*, 1932, **129**, 372.)—The sample of castor oil 135 years old filled a 4-oz. white glass well-stoppered bottle, and was clear, except for a slight white deposit. The taste, at first bland, became hot and burning to the throat. The colour reading in a 1-in. Lovibond tintometer cell was 2·5 yellow and 0·7 red, and the oil had the following characteristics: Sp.gr. at 15·5°/15·5°C., 0·9652; $n_D^{40°}$, 1·4714; optical rotation, + 6·72°; saponification value, 180; iodine value, 82·6; acetyl value, 148·1; acid value, 15·8; and unsaponifiable matter, 0·6 per cent. The oil was soluble in 3·5 parts of alcohol (90 per cent.), and did not solidify or become cloudy at 0° C. The optical rotation was abnormally high, in fact, equal to that of ricinoleic acid itself, and the acidity was high, but, when fresh, the oil would probably have satisfied present-day requirements. D. G. H.

Detection of False "Sponge" Essence of Lemon prepared with Machine-extracted Essence. G. Romeo, N. Galletti and J. Amoroso. (*Giorn. Chim. Ind. Appl.*, 1932, **10**, 397–400.)—Essence of lemon extracted mechanically from the peel is utilised almost exclusively for the preparation of concentrated essence by vacuum distillation. The terpenes and the stearoptene obtained in this operation as secondary products are used for making false "sponge" essence. One such procedure consists in adding to the terpenes a certain quantity (2 to 2·5 per cent.) of the stearoptene recovered as residue of the distillation, citral (2 to 2·5 per cent.), sometimes also esters (0·5 to 1 per cent. of linalyl or geranyl acetate), and sufficient of the mechanically-extracted essence to give to the mixture the straw-yellow or greenish-yellow colour characteristic of "sponge" essence. The ordinary physical constants are insufficient to permit such a product to be distinguished from the genuine material, but this can be done by means of the following procedure: Five c.c. of the essence are evaporated on a water-bath until the odour is no longer detectable, the residue being weighed. This residue is treated with a volume of lemon terpenes (obtained by distilling essence of lemon under reduced pressure and collecting the first 20 or 30 per cent. of distillate) representing in c.c. ten times the weight of the residue in grms. After being mixed with a rod at the ordinary temperature, the mechanical essence gives a clear, and true sponge essence, even after filtration, a turbid solution. Moreover, the difference in refractive index between the lemon terpenes used and the solution containing the stearoptene is from 0·0024 to 0·0035 for the mechanical essence, and from 0·0049 to 0·0060 for sponge essence; expressed as readings on the Wollny (Zeiss) butyro refractometer, these figures are 3·9 to 5·8 in the former, and 8·2 to 10 in the latter case. The same procedure allows of the detection in the false sponge essence of the presence of oils, fats or other substances used either in place of, or together with, the stearoptene. T. H. P.

New Arachis Coffee Substitute. J. Pritzker and R. Jungkunz. (*Z. Unters. Lebensm.*, 1932, **64**, 389–392.)—Analyses as follows are given for the coffee substitute ("Assamba") and for raw and roasted Chinese arachis nuts, respectively:—Moisture, 4·0, 4·7, 1·0; protein, 23·4, 25·0, 28·0; caffeine, 0·4, 0, 0; mineral matter, 2·42, 1·70, 2·00 (insoluble in hydrochloric acid, 0·04, 0 and 0); reducing sugars, 0·4, 0, 0; extract, 17·8, 12·8, 9·0; fat, 34·8, 47·8, 44·5 per cent. (n_D^{40}, 57·5, 55·8, 56·9; acidity, 4·9, 7·6, 2·6); acidity, 8·0, —, 5·6 c.c. *N* NaOH. From these results and from microscopical examination it is calculated that the coffee substitute consists of 33 per cent. of roasted coffee with 5 per cent. of sugar and 62 per cent. of roasted arachis nuts. J. G.

Caffeine in Cereal Beverages. C. H. La Wall and J. W. E. Harrisson. (*Amer. J. Pharm.*, 1932, **104**, 537–539.)—Caffeine, or an infusion or extract of caffeine, or a caffeine-containing ingredient, is sometimes added to cereal beverages. Five brands out of 20 examined in U.S.A., in 1931, contained caffeine in amounts approximating to half a grain to a bottle of the beverage. To detect the caffeine, 100 c.c. of the sample are made slightly alkaline with ammonia and extracted with 25, 15, and successive portions of 10 c.c. of chloroform. The combined extracts are evaporated to dryness, and, if the residue is crystalline, the identification test is applied directly; if not, the residue is purified by the potassium permanganate method of the A.O.A.C. for caffeine in roasted coffee. The identification test consists in adding 15 to 30 mgrms. of potassium chlorate to the dry residue, followed by 1 c.c. of hydrochloric acid. After being mixed the liquid is evaporated to dryness, and a few drops of 10 per cent. ammonium hydroxide solution are allowed to flow over the residue, when the "murexide" purple colour appears in the presence of caffeine. The method may readily be made quantitative.

D. G. H.

Biochemical

Colorimetric Method for the Direct Determination of Urea in Urine. J. F. Barrett and E. B. Jones. (*Biochem. J.*, 1932, **26**, 1246–1250.)—A method for the routine determination of urea in urine is based on the formation of dixanthylurea, a principle described by Fosse (*Compt. rend.*, 1914, **158**, 1076). Interfering substances are removed from the urine with "colloidal iron" (ferric chloride and sodium bicarbonate), and the urea is precipitated from the filtrate by xanthydrol. The precipitate is centrifuged in the presence of barium sulphate, and its nitrogen content is determined colorimetrically after a micro-Kjeldahl digestion. *Reagents required.*—(1) Crystalline ferric chloride in water, 1 per cent. (2) Sodium bicarbonate in water, 0·5 per cent. (3) Barium reagent. Sodium chloride (10 grms.) and sodium sulphate (2 grms.), dissolved in 90 c.c. of distilled water are added to 400 c.c. of glacial acetic acid; 1·2 grm. of barium chloride, dissolved in 10 c.c. of water is added to the mixture. (4) A 2·5 per cent. solution of xanthydrol in glacial acetic acid, kept tightly stoppered, and prepared afresh every few days. (5) Digestion mixture: 100 c.c. of 60 per cent. perchloric acid; 40 c.c. of phosphoric acid (sp.gr. 1·75); 20 c.c. of 3 per cent. sodium selenate solution; 0·5 c.c. of 10 per cent. sodium sulphate solution; 130 c.c. of water. (6) Nessler reagent of Folin and Wu (*J. Biol. Chem.*, 1919, **38**, 81). (7) Ammonium sulphate solution. Pure ammonium sulphate (0·1179 grm.) is dissolved in water, preserved by addition of 2 drops of concentrated sulphuric acid, and diluted to 1 litre. *Procedure.*—To 1 c.c. (or 2 c.c. if the urea-content is low) of urine in a 100-c.c. flask, 2 c.c. of 1 per cent. ferric chloride are added. While the liquid is rotated 10 c.c. of 0·5 per cent. sodium bicarbonate are added, and the whole is diluted to the mark, mixed, and filtered. A suitable amount of filtrate (1 to 5 c.c. depending upon the urea-content) is transferred with an Ostwald pipette to a 4 in. × 1 in. hard glass round-bottomed centrifuge-tube of 35 to 40 c.c. capacity, diluted to 5 c.c. with water, and 5 c.c. of well-mixed barium reagent and 1 c.c. of xanthydrol solution are added. The liquid is mixed and left in a bath of ice-cold water for 20 minutes, mixed again, and the sides of the tube are washed down with 1 c.c. of acetone, which is left on the surface. The tube is centrifuged for five minutes, and the supernatant liquid is decanted, the inverted tube being placed on a sheet of filter-paper for 2 minutes to drain. The excess liquid is removed from the tube by wiping with filter-paper. One c.c. of digestion mixture and a piece of porous earthenware are added, and the tube is gently heated on a sand-bath in a fume cupboard, the mouth of the tube being covered with a watch-glass when heavy white fumes appear and the liquid darkens. Twenty seconds after the brown liquid becomes colourless the tube is removed from the bath, and a few minutes later 20 c.c. of water are added. When the liquid has cooled to room temperature 7·5 c.c. of Nessler reagent are added while the liquid is rotated, and the whole is mixed, and centrifuged for three minutes to remove the precipitate of barium sulphate. The clear supernatant liquid is compared with the standard prepared as follows: Five c.c. of barium reagent and 5 c.c. of water, etc., are placed in a 4 in. × 1 in. tube, centrifuged, drained, and digested as described for the unknown sample. After the liquid has been heated, 15 c.c. of water and 5 c.c. of standard ammonium sulphate solution are added before the addition of 7·5 c.c. of Nessler reagent. The use of a thick blue glass light filter for the comparison in the colorimeter is recommended. *Calculation* (if the standard is set at 20 mm.):

$$\frac{53\cdot6}{\text{Colorimetric reading} \times \text{number of c.c. of filtrate used.}} = \text{grms. of urea per 100 c.c. of urine.}$$

Results show close agreement between the xanthydrol and urease methods.

P. H. P.

Determination of Small Quantities of Oxalic Acid [in Urine]. E. C. Dodds and E. J. Gallimore. (*Biochem. J.*, 1932, **26**, 1242–1245.)—A method is described whereby oxalic acid (in urine) can be quantitatively determined. By a preliminary esterification and distillation *in vacuo* from an acid alcoholic solution the oxalic acid is freed from interfering substances, and can then be precipitated as calcium oxalate and the oxalic acid in the precipitate determined gasometrically. The reagents required are: Alcohol, containing dry hydrochloric acid, *N* solution; lime-water, saturated solution, free from carbonate; ammonium phosphate solution, 0·5 per cent. In a 175-c.c. Claisen flask 25 c.c. of urine + 1 c.c. *N* hydrochloric acid are evaporated almost to dryness *in vacuo* below 50° C., and the flask is then connected with a receiver (a smaller Claisen flask), which contains 13 c.c. of 4 *N* sodium hydroxide solution, and is kept cool by means of a rapid stream of cold water. To the residue in the flask a mixture of 5 c.c. of alcohol and 2 c.c. of benzene is added, the temperature of the water-bath surrounding the distillation flask is raised to 65° C., and the contents of the flask are dried by distilling off *in vacuo* the low-boiling ternary mixture of alcohol, benzene and water. To remove the last traces of water, it is again distilled with 5 c.c. of acid alcohol and 2 c.c. of benzene. The contents of the flask are boiled with 20 c.c. of the alcohol containing acid on a boiling water-bath for half-an-hour; the flask is then reconnected with the receiver, and the contents are distilled *in vacuo* at 65° C. The vacuum reached about the middle of the distillation should be not less than 30 mm. In all, the boiling and distillation are repeated three times. The slightly alkaline solution in the smaller Claisen flask is evaporated to 10 to 20 c.c. *in vacuo*. To free the oxalic acid from the high concentration of sodium chloride an excess of 2 c.c. 5 *N* hydrochloric acid is added, and the solution is extracted with ether in a continuous extractor for six hours. To the ethereal solution 5 c.c. of water are added, and the ether is removed by distillation. The solution is filtered, if necessary, made alkaline to methyl red with *N*/10 sodium hydroxide, and concentrated to about 3 c.c. on a water-bath. The solution of oxalic acid in 3 to 5 c.c. of water in a centrifuge tube is faintly acidified with *N*/10 acetic acid and mixed with 2 c.c. of saturated lime-water. After the mixture has stood for 12 hours at 0° C., 0·5 c.c. of the ammonium phosphate solution is added. The precipitate is centrifuged, decanted, and washed once with 2 c.c. of water. The oxalic acid in the precipitate is then determined by the gasometric method of Van Slyke and Sendroy (*J. Biol. Chem.*, 1929, **84**, 217). The results obtained with urines by the new distillation method are shown to be appreciably higher than those obtained by ether-extraction of the urines. The principle of the method has also been applied to the determination of oxalic acid in blood, from which small quantities of added oxalic acid have been satisfactorily recovered. P. H. P.

Ultra-Violet Absorption of Certain Vegetable or Animal Oils. A. Chevallier, J. Guillot and P. Chabre. (*Compt. rend.*, 1932, **195**, 678–679.)—The ultra-violet spectra obtained through 1 cm. of 1 per cent. solutions in pure hexane of a number of vegetable and fish oils have been examined between λ 2000 and 4000 Å, and the extinction-coefficients plotted as a curve of the form, $\log I_0/I_x = f(\lambda)$. It was found that pure oils of the same type give curves having the same general characteristics, so that it is possible to distinguish, *e.g.*, pure olive oil from pure maize oil. Individual differences in the chemical nature of oils of the same type correspond with characteristic minor variations in the curves as follows:—*Vitamin A* (*e.g.* in cod-liver oils) produces absorption at 3280 Å (*cf.* the work of Morton and Heilbron). *Unsaponifiable matter* absorbs in a zone between 2550 and 2950 Å, corresponding with the presence of sterol and vitamin *D*. *Free fatty acids* are responsible for absorption bands at 3175 Å, between 2825 and 2625 Å (*i.e.* superimposed on a portion of the band due to unsaponifiable matter), and, in particular, bands covering the region from 2550 Å towards the smaller wave-lengths. *Colouring matters* (*e.g.* chlorophyll) are characterised by bands between 4200 and 3300 Å. J. G.

Reaction of Fish-Liver Oils with Antimony Trichloride. F. Ender. (*Biochem. J.*, 1932, **26**, 1118–1123.)—A certain parallelism exists between the biological activity and the intensity of the blue colour given by liver-oil concentrates of halibut (*Hippoglossus hippoglossus*) with antimony trichloride. At room temperature the blue colour thus formed is exceedingly evanescent, but at −40° C. the reaction-product is stable for hours; at −50° C. a heavy blue oil is precipitated on the bottom of the vessel. The author decided to decompose the blue oil at a low temperature according to the following hypothetical equations:

1. Chromogenic substance (vitamin *A* ?) + $SbCl_3$ = blue product.
2. Blue product + H_2O = Chromogenic fraction + SbOCl + 2HCl.

From the results obtained it is concluded that concentrates of halibut-liver oil probably contain two chromogens, of which one is possibly identical with vitamin *A*, and is destroyed by treatment with antimony trichloride and water, whilst the other, which presumably has no connection with growth in animals, still reacts with antimony trichloride, forming a blue product from which the chromogen may be regenerated by the addition of water. The "chromogenic fraction" formed by the addition of water (pieces of ice or an ice-cold mixture of water and 10 per cent. potassium hydroxide for the neutralisation of the possibly harmful hydrochloric acid) to the blue oil was a reddish-yellow oil; with antimony trichloride it gave about one-third of the colour value given by the original concentrate. The results of the biological experiments seem to justify the conclusion that the antimony trichloride reaction is not specific for vitamin *A*; this is in agreement with the findings of Euler and Euler (*Klin. Woch.*, 1930, 916). The absorption bands of the liver-oil concentrate and the "chromogenic fraction," together with the spectra of their reaction products with antimony trichloride, are described. Heilbron, Gillam and Morton (*Biochem. J.*, 1931, **25**, 1352; ANALYST, 1931, **56**, 823) state that the concentrate of halibut-liver oil probably contains two chromogens, of which one causes the absorption at 328*mμ* and that at 583*mμ* of the blue product, and the second causes the absorption at 620*mμ* of the blue product. The author finds that highly active concentrates exhibit with antimony trichloride a decided absorption maximum at 622*mμ*, whereas the inactive preparation (chromogenic fraction) does not, but shows a strong absorption in the neighbourhood of 590*mμ*, and a fainter one at 551*mμ*. On destruction of vitamin *A* subsequent to treatment with antimony trichloride and water, the 622*mμ* band disappears, but the absorption at 590*mμ* is still pronounced. It is, therefore, concluded that an absorption band at 590*mμ* produced by the interaction of antimony trichloride and the "chromogenic fraction" cannot be attributed to vitamin *A*; it is possible, however, that the chromogenic nature of the concentrates after the treatment with antimony trichloride and water may be due to the decomposed vitamin.

P. H. P.

Absorption Spectra of Substances Derived from Vitamin *A*. J. R. Edisbury, A. E. Gillam, I. M. Heilbron, and R. A. Morton. (*Biochem. J.*, 1932, **26**, 1164–1173.)—The blue colour formed in the antimony trichloride colour-test for vitamin *A* is transient. It is possible that the primary process, resulting in the blue colour, leaves the vitamin *A* molecule intact, whilst the secondary reactions associated with the fading of the colour bring about decomposition. The recovery of vitamin *A* from the blue solution by pouring the mixture into much water has been attempted. Partial decomposition of the vitamin occurs, accompanied always by the appearance of narrow absorption bands with maxima at 399, 376, 357 and 340*mμ* (chloroform), and sometimes by additional, less definite maxima, *e.g.* at 425, 324, 308 and 280*mμ*. The wave-lengths at the maxima are constant, irrespective of whether either rich or poor oils or concentrates are used, but the intensities vary roughly with the potency of the material. The oil (or concentrate) obtained is similar in appearance to the original material, and in all cases gives a blue colour with antimony trichloride, similar to, but weaker than, that given by the original. It is claimed that, although the 328*mμ* band cannot be observed as such in the "regenerated" material, its presence, masked by the highly selective absorption of the new products, can be inferred with certainty from the general shape of the absorption curve in conjunction with the results obtained with the colour-test applied to the recovered materials. Recovery of vitamin *A*, although never quantitative, supports the view that the initial reaction is the formation of a vitamin *A* and antimony trichloride loose addition product, but secondary (condensation?) processes probably account for the narrow bands. This view is supported by the observation that the similar maxima 392, 369, 350, 333*mμ* (alcohol) can be obtained with greatly enhanced definition by the action of alcoholic hydrogen chloride on rich concentrates, the intensity, persistence, rate of development and permanence depending on the concentration of hydrogen chloride. Even under optimum conditions the reaction is incomplete, and the product unstable in acids. Neutralisation of the acid with sodium ethoxide arrests the decomposition of the material, but does not effect reversal to vitamin *A*. Similar narrow bands, together with a broad continuous band with its maximum at 290$m\mu$, are shown in certain fractions obtained in slow high vacuum distillation of rich concentrates heated to about 180° C. By prolonged heating at 120 to 125° C. in an atmosphere of nitrogen the development of narrow bands could not be induced to more than a minute extent, but the vitamin nevertheless decomposed fairly readily, the main product exhibiting a maximum at 290$m\mu$. In alcohol at the boiling-point, vitamin *A* is unexpectedly stable to prolonged exposure to a stream of oxygen. After some hours, the 328$m\mu$ maximum decreases in intensity, the absorption in the region 260 to 300$m\mu$ slowly increases, and the narrow absorption bands in the near ultra-violet appear, but with comparatively brief persistence. Ozonised oxygen rapidly destroys vitamin *A* with disappearance of selective absorption, but compounds with maxima at 290$m\mu$ and 272$m\mu$ can be detected in the very early stages. The data are consistent with the vitamin *A* molecule containing a side chain with at least four double bonds, which can be attacked in turn by ozone to give products with broad bands. The hypothesis of ring closure to give hydronaphthalene derivatives as an explanation of the narrow bands will be discussed in a later communication. P. H. P.

Isomerisation of Carotene by Means of Antimony Trichloride. A. E. Gillam, I. M. Heilbron, R. A. Morton, and J. C. Drummond. (*Biochem. J.*, 1932, **26**, 1174–1177.)—The stable blue solution (λ maximum 583 to 590$m\mu$), obtained by the action of antimony trichloride on carotene in chloroform, was poured into water and the organic matter recovered free from antimony. Antimony oxychloride was precipitated and the original colour of the carotene returned. The oxychloride was dissolved in the minimum quantity of concentrated hydrochloric acid, and the mixture was left to stand, when the chloroform layer gradually separated. Red crystals were isolated from the chloroform layer; the melting-point of the purest specimen of crystals obtained was 185° C. The absorption spectrum of the recovered product has been determined in chloroform and carbon disulphide. In both the visible and ultra-violet regions it is quite different from that of carotene. The properties of the substance agree with those of *iso*carotene. P. H. P.

Toxicological and Forensic

Distribution of Chloral Hydrate in the Organism. N. E. Renescu and B. B. Olzsewski. (*Compt. rend.*, 1932, **195**, 624–626.)—Chloral hydrate in 10 per cent. solution was administered, by way of the internal saphenous vein, to dogs (0·25 to 1 grm. per kilo.), and, after death, was found in relatively large quantities in all the organs, and particularly in the brain, liver, kidney, heart and intestines. Chloroform was present in some cases, but only in traces, so that no strong support was obtained for the theory that the narcotic action of chloral hydrate is due to chloroform produced by decomposition. The chloral hydrate content of the blood is relatively high after injection and then decreases rapidly; that of the liver and adipose tissue increases with the duration of narcosis, whilst that of the brain does not appear to be related either to this factor or to the magnitude of the dose. After 2 to 3 months of putrefaction no chloral hydrate remains in the organs. *Chloroform* was determined by distilling 20 grms. of the disintegrated sample with 100 c.c. of 95 per cent. alcohol and 10 c.c. of 20 per cent. tartaric acid into a little 95 per cent. alcohol. The distillate (50 c.c.) was allowed to stand in a stoppered flask for 24 hours with 10 c.c. of a 10 per cent. solution of potassium hydroxide in alcohol, and hydrolysis was then completed by heating for 30 minutes on the water-bath. The chlorides in a solution, in 5 c.c. of dilute nitric acid, of the residue after evaporation, were then titrated with 0·05 *N* silver nitrate solution (1 c.c. $\equiv$ 1·99 mgrm. $CHCl_3$). *Chloral hydrate* was determined by distillation of the sample with 140 c.c. of water and 20 c.c. of the solution of tartaric acid. When a few drops of distillate no longer gave the resorcinol reaction, a portion (40 c.c.) was saponified by the action of 20 c.c. of the alkali in the presence of 60 c.c. of 95 per cent. alcohol for 24 hours in the cold, followed by 3 hours on the water-bath; after titration in nitric acid solution as before and deduction of any value corresponding with the chloroform-content, 1 c.c. of 0·05 *N* $AgNO_3 \equiv$ 2·76 mgrms. of chloral hydrate. J. G.

Devonshire Colic (Lead Poisoning) due to Cider. M. C. N. Jackson and L. N. Jackson. (*Lancet*, 1932, **223**, 717–719.)—The relation between this disease and the consumption of cider containing lead has been recognised since 1767, at which time much lead plant was used in the preparation of this beverage. In addition, the acidity of the product was "corrected" by the addition of metallic lead, litharge or lead acetate. A recent outbreak of Devonshire colic, involving ten cases (males), was traced to contamination of the cider supplied at six public-houses with lead in quantities varying from 1/10th to 1/20th grain per gallon. The cider in the casks in which it was delivered was free from lead, but, when received from the nozzles of the counter engines, contained the amounts recorded above. The source of the metal was the lead pipes connecting the casks and the engines, and similar results were obtained whether these pipes were tinned internally or not. As anticipated, the portions of cider which remained in the pipes overnight were most heavily contaminated. The analyses were carried out by destruction of the organic matter with sulphuric and nitric acids (*cf.* Wilkie, *J. Soc. Chem. Ind.*, 1909, 636), the determination being completed by the addition of sodium sulphide and comparison of the colour obtained with that yielded by known amounts of lead. T. J. W.

Agricultural

Determination of Cellulose in Soil. J. A. Daji. (*Biochem. J.*, 1932, **26**, 1275–1280.)—During the course of an investigation into the decomposition of green manures in soil it was necessary to determine the amount of cellulose that underwent changes at the different stages of fermentation. A method has, therefore, been devised, and is described for the determination of cellulose in soil mixed with plant materials. It is essentially a combination of the methods of Jenkins (*Biochem. J.*, 1930, **24**, 1428) and Charpentier (*Meddel. No.* **205**, *Centr. Forsök. Jord. Bakter. Avdel.*, No. 22, 1920). The soil is treated with hot dilute alkali and acid, and then with a solution of sodium hypochlorite in the cold. Cellulose is then extracted from the residue with Schweitzer's reagent, precipitated with alcohol, and determined by loss of weight on ignition. The results obtained by this method on plant materials alone agree very closely with those given by the hypochlorite method of Jenkins. It is shown that it is necessary to remove the lignin from the plant tissues, otherwise it is not possible to obtain a quantitative yield of cellulose by extraction with Schweitzer's reagent. When different plant materials are mixed with soil, almost the whole of the cellulose added is recovered by the method, but a small part is retained by the soil, and is not extracted by the Schweitzer's reagent. This loss of cellulose was also observed by Charpentier and others, and was attributed by them to adsorption by the soil. No attempt has been made to apply the method to different types of soil. P. H. P.

Water Analysis

Determination of Hydrogen Sulphide in Industrial Waters. Kapp. (*Compt. rend.*, 1932, **195**, 608–610.)—Since at ordinary temperatures the oxygen dissolved in 1 litre of gas-washing water may oxidise about 18 mgrms. of hydrogen sulphide in 1 hour, or in less time if traces of iron are present, the iodimetric determination has been modified as follows:—To 500 c.c. of sample are added, as soon as possible, about 20 c.c. (an excess) of a 20 per cent. solution of cadmium sulphate; since the resulting cadmium sulphide is not appreciably oxidised, the analysis may be interrupted, *e.g.* for the sample to be taken from the works to the laboratory. The mixture is then heated to boiling in a flask provided with a tap-funnel and a delivery tube leading through a vertical coil-condenser into a known quantity of a solution of iodine, and 100 c.c. of a cool mixture of equal volumes of water and sulphuric acid are added slowly. Ten minutes after the disappearance of the colour of the sulphide the distillation is stopped, and the excess of iodine is titrated with sodium thiosulphate solution. If the sample is large (*e.g.* when the hydrogen sulphide content is small), the cadmium sulphide may be removed by filtration and added with the filter to 500 c.c. of water in the flask. J. G.

Organic Analysis

Determination of Fluorine and Boron in Organic Compounds. D. J. Pflaum and H. H. Wenzke. (*Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 392–393.)—About 0·5 grm. of the substance is weighed in a gelatin capsule and placed in the cup of a Parr sulphur bomb of the electrical ignition type. A mixture of 10 grms. of sodium peroxide, 1 grm. of potassium chlorate and 0·5 grm. of sugar is added, the bomb is closed tightly, and the mixture is ignited. Pure iron wire is used for the fusion wire. The bomb is allowed to become quite hot, then cooled in water, opened, and the contents of the cup are dissolved in warm water. The solution is boiled and filtered, and the filtrate is boiled with the addition of 15 grms. of ammonium chloride until ammonia vapours are no longer evolved; this requires about two hours. The hot solution, filtered, if necessary, is treated with 10 c.c. of 2 N calcium nitrate solution and boiled, 1 c.c. of ammonia is added, the mixture is cooled, and the precipitate is collected on a filter, washed with water (not more than 50 c.c.), dried, ignited in a platinum crucible and weighed as CaF_2. Sufficient sodium hydroxide solution is added to the filtrate to produce a precipitate of calcium hydroxide and carbonate, the mixture is boiled until all ammonia is expelled, and filtered, and the filtrate is diluted to 250 c.c. Fifty c.c. of this solution are titrated with 0·1 *N* hydrochloric acid, methyl-orange being used as indicator; the remaining 200 c.c. of the solution are then neutralised by adding the requisite volume of 0·1 *N* hydrochloric acid, but no indicator; after the addition of mannitol and phenolphthalein solution, the mixture is titrated with 0·1 *N* sodium hydroxide solution, and the result is calculated in terms of boron. W. P. S.

Determination of Ethylene Oxide. O. F. Lubatti. (*J. Soc. Chem. Ind.*, 1932, **51**, 361–367.)—By means of Deckert's method of determining ethylene oxide, in which the oxide is converted into the chlorohydrin (*Z. anal. Chem.*, 1930, **82**, 297), it is not found possible to account for more than 94 per cent. of the oxide. When various modifications, particularly the use of magnesium chloride in place of sodium chloride, are introduced the method will, however, give results which are satisfactory and in agreement with those of Müller's dichromate method (*Chem.-Ztg.*, 1920, **44**, 573). The following modified form of this dichromate method is proposed: Use is made of a stout, thick-walled, flat-bottomed flask, holding about 400 c.c. and provided with a well-fitting ground-in stopper. The mouth of the flask expands into a flange for preventing loss of liquid during rinsing, and the stopper extends into a pointed tip to facilitate draining. Fifty c.c. of sulphuric acid (1:3) are pipetted into the reaction flask, which is left in a bath at 70° C. for 10 minutes and then removed. After the introduction of a tube of ethylene oxide (0·15 to 0·2 grm.), the flask is quickly stoppered, inverted and shaken until the tube is broken, and then shaken for 1 minute and allowed to cool slowly. After about 15 minutes, the stopper is removed and rinsed, and the open flask is again heated at 70° C. for 10 minutes, and afterwards cooled under the tap. With the help of a dry funnel, exactly 5·5720 grms. of "A.R." potassium dichromate (previously dried for 3 hours at 130° C.) are added, the funnel being rinsed with 25 c.c. of sulphuric acid (1 : 3) to remove adherent dichromate. The flask is heated gradually on a wire gauze over a small flame and kept gently boiling for 20 to 25 minutes, being swirled, at frequent regular intervals, to prevent loss by spurting. The liquid is then cooled to the laboratory temperature and made up to 500 c.c. with water in a measuring flask. Twenty-five c.c. of the solution, 400 c.c. of water, 25 c.c. of sulphuric acid (1 : 3), and 20 c.c. of 10 per cent. potassium iodide solution are introduced in order into a litre flask, the mixture being then titrated with thiosulphate solution (28·3 grms. per litre) in presence of starch. Concurrently with this determination, a blank without the oxide is carried out similarly. One c.c. of the dilute dichromate solution corresponds with 0·001 grm. of ethylene oxide.

When the modified Deckert method is employed for determining the ethylene oxide in a fumigated space, use is made of a special flask, devised by Page (*J. Soc. Chem. Ind.*, 1932, **51**, 369T). This flask, of 1-litre capacity, is fitted with a rubber stopper (covered with castor oil), carrying an exhaustion tube and a capillary gas-inlet, to which a small reservoir is attached inside the flask. Ten grms. of solid magnesium chloride ($+6H_2O$) and 50 c.c. of saturated magnesium chloride solution are introduced into the flask, and 5 c.c. of 0·5 *N* sulphuric acid into the reservoir. The stopper is inserted and the flask is evacuated, sealed, and tilted to allow the sulphuric acid to mix with the magnesium chloride solution. The gas-charge is then introduced, and the flask is well shaken for 30 seconds. The stopper with its fittings is well washed with 25 to 30 c.c. of water into a tall 150-c.c. beaker, the washings and the liquid in the flask being titrated together with 0·05 *N* sodium hydroxide solution in presence of methyl-orange; the first change to orange is taken as the end-point. A parallel test, without the gas containing ethylene oxide, is made in exactly the same manner: 1 c.c. of 0·05 *N* NaOH $\equiv$ 2·202 mgrms. of C_2H_4O. T. H. P.

Test for Oxalic Acid. E. R. Caley. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 445.)—A solution of 0·1 grm. of the acid in 2 c.c. of water is treated with 1 c.c. of 6 *N* sodium hydroxide solution and the mixture is shaken for two minutes. The formation of a white crystalline precipitate indicates oxalic acid. The following acids do not yield a precipitate, even when present in larger quantity than 0·1 grm.; citric, crotonic, glycollic, maleic, malic, malonic, mandelic, succinic, and tartaric. Dihydroxytartaric acid gives a precipitate in the test, but this acid is unstable and not readily obtained. W. P. S.

Essential Oil of *Dacrydium cupressinum*. M. S. Carrie. (*J. Soc. Chem. Ind.*, 1932, **51**, 367–368T.)—This oil, obtained by steam-distillation of the leaves and afterwards dried, was found to consist almost entirely of hydrocarbons, and to give three well-marked fractions when distilled under reduced pressure: (1) A terpene fraction (20 per cent.), consisting almost entirely of α-pinene; McDowall and Finlay (*ibid.*, 1925, **44**, 42T) found no terpenes. (2) A sesquiterpene fraction (9·4 per cent.), b.pt. 132 to 135° C./20 mm., sp.gr. 0·9238 at 20/20° C., n^{20}_{D} 1·5010 (1·4990 after two distillations over sodium), $[\alpha]_D + 17·57°$; catalytic hydrogenation, using palladium as catalyst, shows that the compound is tricyclic, the double linking being probably in the nucleus. (3) A liquid diterpene fraction, giving as a well-marked sub-fraction (31 per cent. of the oil), a green, highly viscous oil, b.pt. 150 to 154° C./1 mm., sp.gr. 0·9763 at 15°/15° C., n^{15}_{D} 1·5211, $[\alpha]^{15}_{D} + 15·17°$; hydrogenation and ozonolysis (which yielded formaldehyde) indicate the presence of 0·85 of a double linking in a side-chain, and it is assumed that the fraction represents a constant-boiling mixture of 85 per cent. of a tetracyclic diterpene with 15 per cent. of a saturated one. Only partial separation of these two was accomplished by fractionation of the hydrogenated product, and oxidation by permanganate of a waxy product formed, with the formaldehyde, on ozonolysis gave an acid of the probable formula $C_{14}H_{21}O.CO_2H$. McDowall and Finlay's solid diterpene, which was not found during the present examination, proves to be unsaturated, as it decolorises bromine in chloroform or absolute alcohol solution, although it does not do so in ether or carbon disulphide. T. H. P.

Chemical Examination of the Marking Nut. P. P. Pillay and S. Siddiqui. (*J. Indian Chem. Soc.*, 1931, 8, 517–525.)—The black corrosive juice of the pericarp of the nut of the marking nut tree (*Semecarpus anacardium*, Linn.) is administered internally with emollient oils, and is of great medicinal value, besides being used in admixture with lime as an indelible marking ink. Anacardic acid, cardol, catechol and anacardol were not present, but the following substances were isolated from the black pericarp juice (of which 28 to 36 per cent. was obtained):—(1) "Semecarpol" a monohydroxyphenol boiling at 185–190° C. at 2·5 mm., solidifying below 25° C. to a fatty mass, and forming 0·1 per cent. of the extract; (2) "Bhilawanol," a *o*-dihydroxy compound, $C_{21}H_{32}O_2$, distilling at 225°–226° C. at 3 mm., solidifying below 5° C., and forming 46 per cent. of the juice; and (3) a tarry corrosive residue yielding no identifiable compound. Work on bhilawanol finally established the identity of the hydrogenation product, hydro-bhilawanol, with hydro-urushiol the hydrogenation product of uroshiol the chief constituent of Japan lacquer, the dried juice of *Rhus vernicifera*, and this parallel may eventually lead to the extension of the utility of each plant. The experimental work is described in detail. D. G. H.

Determination of Gum in Petrol. M. J. Mulligan, W. G. Lovell and T. A. Boyd. (*Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 351–356.)—Fifty c.c. of the petrol are placed in a glass beaker fitted in a bath containing a liquid (*e.g.* ethylene glycol) boiling at about 200° C. Air flowing at the rate of 1 litre per second and heated by passing through a coil in the bath is used to evaporate the petrol and dry the residual gum. About twenty-five minutes are required to obtain a residue of gum of substantially constant weight. Oxidation during the evaporation and drying does not introduce appreciable error. W. P. S.

Inorganic Analysis

Use of Metallic Lithium in the Determination of Nitrogen, etc., in Inert Gases. J. H. Severyns, E. R. Wilkinson and W. C. Schumb. (*Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 371–373.)—A method for the determination of nitrogen, oxygen and water vapour in helium depends on the fact that metallic lithium forms non-volatile compounds with the impurities mentioned. The apparatus used consists of an inverted 400-c.c. round-bottomed flask fitted with three capillary taps which are sealed to the bottom of the flask; one leads to a manometer, another to a vacuum pump, and the third to the source of the gas sample. An electrical heating device, carrying a small iron boat is fitted into the flask by means of a glass tube and rubber stopper. A small piece of lithium is placed in the boat, the flask is exhausted, and the gas (helium) to be analysed is admitted slowly until the pressure reaches, say, 550 mm. Current is then supplied to the heating device, the lithium is melted, and rapid absorption of the oxygen and nitrogen takes place. Although water-vapour is also absorbed, this takes some time, and it is preferable to dry the helium previously. After about two minutes the heating is stopped and, when the apparatus is cold, the pressure is re-determined. The second pressure, divided by the first, gives the fractional purity of the sample. At ordinary temperature lithium does not react with oxygen, nitrogen or water-vapour within a period of five minutes. W. P. S.

Volumetric Analysis involving the use of Liquid Amalgams. S. Kaneko and C. Nemoto. (*J. Soc. Chem. Ind. Japan*, 1932, **35**, 343B.)—The following two simplified forms of Nakazono's method of volumetric analysis, in which liquid amalgams are used (*J. Chem. Soc. Japan*, 1921, **42**, 36), have been devised. (1) A portion of the sample solution, acidified with sulphuric acid and diluted to a known volume, is reduced by shaking for a few minutes in an 80-c.c. stoppered flask with 150 grms. of dry zinc, cadmium or bismuth amalgam, and 25 c.c. of the reduced solution are withdrawn and titrated with standard potassium permanganate solution. Amalgam for this purpose may be obtained in a dry condition from the stock of amalgam, which is ordinarily preserved under dilute sulphuric acid, by separation in the apparatus shown in Fig. 1, A and B being the outlets for dry amalgam and the acid preserving liquid respectively.

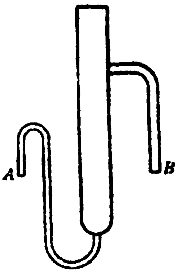


Fig. 1

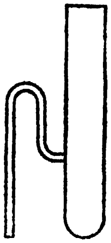


Fig. 2

(2) Twenty-five c.c. of the sample solution are shaken, as above, with 150 c.c. of the amalgam, which need not be dry. The whole is poured into an apparatus, as shown in Fig. 2, the aqueous liquid being received from the side tube in a separate vessel; the amalgam is well washed, the washings being similarly collected, and the combined liquids are titrated. S. G. C.

Determination of Antimony in Copper. H. Blumenthal. (*Z. anal. Chem.*, 1932, **90**, 118–121.)—A criticism of Boehm and Raetsch's paper (ANALYST, 1932, 538). It is observed that these authors added antimony in the form of a lead alloy to pure copper, the antimony being precipitated as lead antimonate when the nitric solution was treated with excess of ammonia. Quantitative recovery of the antimony was actually achieved without the use of iron, by adding 1·5 grm. of lead nitrate to the solution of 25 grms. of copper and precipitating with ammonia. In the analysis of bronze, the small amounts of antimony present are occluded in the relatively large precipitate of stannic acid; in the subsequent ammonia precipitation the ferric hydroxide present merely assists the filtration of the stannic acid. W. R. S.

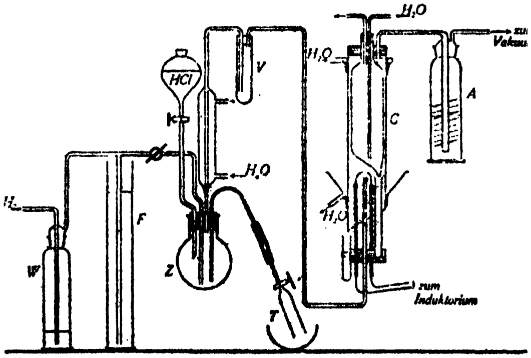
Determination of Thallium after Oxidation with Bromine. E. Browning. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 417.)—Thallous salts are oxidised readily when their solutions are treated with a slight excess of bromine; subsequent addition of ammonia causes precipitation of thallic hydroxide, which may be collected, dried at 150° to 200° C., and weighed. Qualitatively, 0·1 mgrm. of thallium in 10 c.c. of solution may be detected by the dark coloration of the thallic hydroxide.

W. P. S.

Rapid Colorimetric Determination of Nickel in Copper Alloys. V. P. Ochotin and A. P. Sytschoff. (*Z. anal. Chem.*, 1932, **90**, 109–111.)—The alloy (0·01 to 0·015 grm. for a 20 : 80 nickel-copper alloy) is dissolved in 10 c.c. of nitric acid, the solution is diluted to 25 c.c., and sufficient ammonia is added to convert the copper into the deep-blue ammine compound. The solution is treated with 15 c.c. of 1 per cent. dimethylglyoxime solution, and the liquid is cooled in a separating funnel and shaken with 15 c.c. of ether, which extracts the nickel precipitate, forming a suspension. The aqueous layer is removed, and the ether is washed twice with water and transferred to a colorimeter tube. After addition of 5 c.c. each of alcohol and of collodion to stabilise the suspension, the colour is matched against that obtained with a standardised sample. A determination can be made in 10 minutes. The suspension is stable for about 24 hours.

W. R. S.

Determination of Phosphorus in Aluminium. W. D. Treadwell and J. Hartnagel. (*Helv. Chim. Acta*, 1932, **15**, 1023–1029.)—A new micro-method is proposed by which as little as a few thousandths of one per cent. of phosphorus may be determined in aluminium or aluminium alloys. In outline, the aluminium is dissolved in acid in an atmosphere of hydrogen, and the phosphorus, liberated as phosphine with the hydrogen evolved, is oxidised by combustion, the phosphoric acid produced being collected and the phosphorus determined by the "molybdenum-blue" reaction. The apparatus required, which is shown in the diagram, is self-explanatory except for the combustion chamber, C. This is virtually a double-surface condenser, open at the bottom and consisting of an outer glass cylinder, about 25 cm. × 5 cm. in diameter, cooled by an external stream of water, and an internal vessel of special shape through which water is circulated. Projecting upwards into the combustion chamber are (*a*) the hydrogen leading tube, which terminates in a quartz capillary, 3 cm. × 0·5 mm. in diameter, to act as the burning jet; (*b*) platinum points connected to an induction coil, by means of the



sparks from which the issuing hydrogen is ignited in air which is drawn up, at a rate of about 1 litre per minute into the chamber, by means of the vacuum pump connected to A; two glass test-tubes are provided for collecting the condensed liquid from the two condensing surfaces. *Method.*—The sample of aluminium (0·1–1 grm., containing 1–60γ of phosphorus) is placed in the 100-c.c. decomposition flask, Z. Hydrogen is passed into the apparatus from a cylinder at about 160 c.c. per minute, as judged by the rate of bubbling in the water wash-bottle, W (the cylinder, F, is a pressure-regulator). The hydrogen is ignited, by sparking, at the quartz jet in C, and the height of the flame is adjusted to 6–8 mm. by regulating the admission of hydrogen into the apparatus. The solution of the sample in Z is effected by slowly dropping 10 per cent. hydrochloric acid from the dropping funnel at a rate so regulated that the dissolution occupies 20 to 40 minutes (the purpose of funnel, T, is to enable, if necessary, water to be introduced into the flask to reduce a possibly violent rate of solution, or exhausted acid to be withdrawn). Hydrogen is passed for 15 minutes after solution is complete, in order to sweep out the apparatus. The interior of the combustion chamber is finally rinsed out with water, and the condensate and washings, together with 1 or 2 drops of dilute sulphuric acid are evaporated in a platinum dish to a volume of about 10 c.c. The phosphorus-content of the liquid is determined by the "molybdenum-blue" method of Zinzadze (ANALYST, 1932, 411). It is stated that the phosphoric acid produced in the combustion of the phosphine is completely absorbed by the condensed water in the combustion chamber. S. G. C.

Separation of Beryllium from other Elements by Guanidine Carbonate. A. Jílek and J. Kota. (*Z. anal. Chem.*, 1932, 89, 345–354.)—The method for the separation of beryllium from aluminium, described in an earlier paper (ANALYST, 1932, 406), can be used without modification for the separation of beryllium from ferric, uranyl, thorium, zirconium, copper, antimony, and thallium salts, and from chromic, molybdic, and arsenious acids. For the separation of beryllium from vanadic and tungstic acids, the weakly acid solution, after addition of the ammonium tartrate solution, should next be treated with a slight excess of caustic alkali, and then neutralised with dilute acid against methyl red. Guanidine carbonate reagent and formaldehyde are then added as in the original method. If this modification is not adopted, a little vanadic or tungstic acid finds its way into the beryllium precipitate. W. R. S.

Use of α-Benzoinoxime in the Determination of Molybdenum. H. B. Knowles. (*Bur. of Standards J. Research*, 1932, 9, 1–7.)—α-Benzoinoxime, which has been proposed as a specific precipitating agent for copper in ammoniacal solution by Feigl (*Ber.*, 1923, 56(ii), 2083), has been found to precipitate molybdenum quantitatively in acid solution and to provide a separation of molybdenum from many other elements. *General Method of Determination.*—The test solution should contain 10 c.c. of concentrated sulphuric acid and not more than 0·15 grm. of sexavalent molybdenum in 200 c.c. The solution is cooled to 5–10° C., and 5 c.c. of a 2 per cent. solution of α-benzoinoxime in alcohol for each 0·01 grm. of molybdenum present, with 10 c.c. extra, are added with stirring. Just sufficient bromine water to colour the solution a pale yellow is added, followed by a few c.c.

of the precipitating agent. The liquid is kept cooled 10–15 minutes, and is stirred occasionally. A little macerated filter-paper pulp is then stirred in, and the liquid is filtered through a filter-paper of close texture. The precipitate is washed with 200 c.c. of a cold, freshly-prepared solution containing 25 c.c. of the 2 per cent. alcoholic benzoinoxime solution and 10 c.c. of concentrated sulphuric acid per litre. The precipitate and paper are dried in a weighed platinum crucible, charred without flaming, ignited to constant weight at 500–525° C., and weighed as molybdenum trioxide. Good results were obtained in test experiments with 0·001 to 0·1 grm. of molybdenum present. The limits of the amount of reagent to be added would appear to be fairly critical, *viz.* from two to five times the theoretical (1 atom of molybdenum to 3 mols. of benzoinoxime), since incomplete precipitation resulted either (1) when slightly more than the theoretical or (2) when ten times the theoretical amount of reagent was used. Low results were obtained when the time specified for the precipitation was exceeded. Wide variations in the degree of acidity of the test solution are permissible, good results having been obtained, *e.g.* with solutions containing (*a*) acetic acid buffered with acetate, (*b*) up to 20 per cent. of sulphuric acid; solutions containing 5 per cent. of hydrochloric or nitric acid were successfully used when the presence of sulphuric acid was objectionable, *e.g.* in the presence of lead; phosphoric acid was found unobjectionable, but incomplete precipitation was obtained in presence of tartaric acid; hydrofluoric acid must be absent. A detailed survey of the behaviour of most other elements with the reagent indicated that the only elements besides molybdenum giving precipitates in mineral acid solutions are tungsten, palladium, sexavalent chromium and quinquevalent vanadium; tervalent chromium and quadrivalent vanadium cause no interference; niobium and silicon interfere by being partially precipitated with molybdenum.

The following applications of the method to commercial products were used by the author:

Molybdenum Steel.—One grm. was dissolved in 50 c.c. of dilute sulphuric acid (1 + 6) and oxidised with the minimum of nitric acid. The filtered solution was diluted to 100 c.c., and sufficient ferrous sulphate solution was added to reduce vanadic and chromic acids; it was cooled to 5–10° C., and the precipitation with α-benzoinoxime carried out as already described. The ignited oxide was examined for any "insoluble residue" and for tungsten. Test results cited of determinations of molybdenum in standardised chromium-molybdenum steels and in solutions of plain steel containing added molybdenum show fairly good agreement with the amount present. [*Abstractor's note:* The process would appear to be inapplicable, without modification, to steel containing much tungsten.]

Calcium molybdate, Wulfenite and Molybdenite Ore.—To the solution obtained by decomposing 0·2 to 0·5 grm. of the material with hydrochloric acid, or with nitric acid and bromine, followed by evaporating "to fumes" with 10–15 c.c. of sulphuric acid, dissolving the residue in 100 c.c. of water, and filtering (a small quantity of molybdenum was found in the insoluble residue by a colorimetric test made on the solution after fusing the residue with sodium carbonate), sufficient potassium permanganate was added to produce a permanent pink colour. Sulphurous acid was added to reduce any vanadic or chromic acid present, and the excess was removed by boiling. The benzoinoxime precipitation, as already described, was then carried out. The ignited and weighed impure molybdic oxide obtained was dissolved in the minimum of ammonia, and the insoluble residue was filtered off and ignited. The ammoniacal extract was acidified with hydrochloric acid, cinchonine was added to precipitate the tungsten present, and the liquid was kept overnight; the precipitate of cinchonine tungstate was then filtered off, washed, ignited at 525° C., and weighed. The weight of this tungstic oxide, together with that of the residue insoluble in ammonia, was deducted from the weight of the impure molybdic oxide. Good results were obtained in test experiments.

S. G. C.

Composite Reagent for Calcium. G. J. Cox and M. L. Dodds. (*Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 361.)—The reagent is prepared by dissolving 200 grms. of crystallised oxalic acid and 500 grms. of ammonium chloride in 3500 c.c. of water, adding 1000 c.c. of glacial acetic acid and 10 c.c. of 0·04 per cent. methyl-red solution, and filtering the mixture. For the determination of calcium in bone-ash, or similar material, the ash is dissolved in dilute hydrochloric acid, a suitable quantity of the reagent is added, the mixture is boiled, and ammonia is added until the reaction is slightly alkaline to methyl-red. W. P. S.

Determination of Potassium as Chloroplatinate. R. Strebinger and H. Holzer. (*Z. anal. Chem.*, 1932, 90, 81–86.)—The authors prove, in a series of tests, that alcohol containing acetaldehyde causes slightly low results in the determination of potassium as chloroplatinate, this being ascribed to partial reduction. Alcohol free from aldehyde is recommended. W. R. S.

Microchemical

Microchemical Reactions with Loretin. C. Van Zijp. (*Pharm. Weekblad*, 1932, 69, 1191–1197.)—Loretin (2-iodo-1-hydroxyquinoline-4-sulphonic acid) is a stable reagent which gives highly anisotropic crystals with a number of metals, the microscopical characteristics of which sometimes allow the simultaneous detection of two different metallic salts. It is used medicinally in admixture with 20 per cent. of sodium bicarbonate ("yatren"). The ordinary technique of a drop-reaction is used, but in some cases it is necessary to hold the watch-glass containing the mixture over a vessel containing ammonia. Orange needles are obtained with barium and strontium carbonates, and with calcium phosphate, carbonate and chloride. Colourless needles (often radiating) are produced with sodium chloride, lithium carbonate (readily soluble in water), nickel and cadmium chlorides, copper acetate and sulphate, and also under certain conditions, with calcium and strontium carbonates (*vide supra*). Magnesium sulphate and oxide deposit slowly, on scraping the glass, highly anisotropic crystals having a principal angle of 74°, and similar to those obtained with zinc oxide, chloride and sulphate, and with manganese sulphate and carbonate. Ferrous sulphate and lactate give hexagonal crystals, whilst cobalt acetate gives a precipitate of indefinite structure. Mercurous, mercuric, potassium, ammonium, rubidium and caesium chlorides, magnesium, barium, calcium and strontium sulphates, iron salts, calcium oxalate, aluminium, bismuth and silver nitrates, lead acetate and carbonate, potassium antimonyl tartrate, zinc sulphide, uranyl acetate, sodium uranate and bismuth hydroxide give negative results. Applications to the detection of dolomite, of zinc in white lead, and of calcium in magnesium carbonate are described. J. G.

Chemical Identification of Foreign Substances in Metals and Alloys. M. Niessner. (*Mikrochem.*, 1932, 12, 1–24.)—The "spot" methods of Feigl are used to identify foreign elements on metallic surfaces. An imprint of the surface is taken on gelatin paper, and the test is carried out on the paper. The metallic surface is first polished, and the impregnated gelatin paper (similar to that used in photography, and free from contamination), with a smooth surface, is placed on the metal and pressed down. The gelatin is impregnated with a suitable reagent, according to the element sought. In order to prevent drying of the gelatin paper, a piece of damp filter-paper, also impregnated with the reagent, is placed behind it. For very small pieces of metal the gelatin is mounted on a sheet of glass, and the metal is pressed on to the gelatin. The metal and gelatin paper should stay in close contact for 5 minutes. The paper is then carefully removed, and should show a mirror-image of the positions of the element in question on the metal. Where the colour has to be developed, as when the colour change takes place in alkaline solution, and the gelatin has been pressed to the metal while impregnated with acid solution, the paper should be immersed in the correct developer until the colour appears. When very acid solutions are necessary for the solution of the surface, stiff filter-paper must be substituted for gelatin paper. Examples of the detection of sulphur, of phosphorus, and of oxidising substances in iron and steel (with photomicrographs) are given, and the detection of copper, cobalt and nickel, separately, together, and in alloys, is described. J. W. B.

Application of Sodium Diethyldithiocarbamate Reaction to the Micro-Colorimetric Determination of Copper in Organic Substances. W. D. McFarlane. (*Biochem. J.*, 1932, 26, 1022–1033.)—An examination of the reaction between copper and sodium diethyldithiocarbamate, discovered by Delépine (*Compt. rend.*, 1908, 146, 981) and developed by Callan and Henderson (ANALYST, 1929, 54, 650), was undertaken with the object of devising more accurate methods for the determination of copper in organic materials in studying the rôle of copper in metabolism. The examination has revealed certain points of importance in the quantitative application of the reaction: A. The golden-brown copper salt formed is much more soluble in amyl alcohol than in water. The coloured copper salt can be rapidly and quantitatively extracted from aqueous solution by amyl alcohol. The reaction may then be applied over a much wider range of copper concentration. B. The golden-brown colour is intensified in the organic solvent; thus the sensitivity of the reaction is increased. C. The depth of colour is directly proportional to the amount of copper present, provided that the range of copper concentrations is not too great. D. In alkaline solution, ferric pyrophosphate does not give the reaction, but the reactivity of the copper is unimpaired; therefore, in alkaline pyrophosphate solution copper may be determined in the presence of iron. E. The oxidation of cupric sulphide in the cold with saturated bromine water and 10 per cent. sulphuric acid does not interfere with the subsequent application of the colour reaction. These observations have been utilised in the development of procedures, by means of which copper may be accurately determined in biological materials. Blood, milk, liver, crude glutamic acid and crystalline haemoglobin have been analysed for copper, and the method used is described in each case. A sample of crystalline haemoglobin of unknown origin was found by the carbamate reagent to contain only 0·0057 mgrm. of copper per grm. of haemoglobin. P. H. P.

Electrical Micro-Determination of Mercury. F. Patat. (*Mikrochem.*, 1932, **11**, 16–21.)—The method, which is suitable for small amounts of mercury down to 0·15 mgrm., gives results which differ from the calculated amount by 0·004 mgrm. or less. Metallic mercury is dissolved in a small volume (0·5 to 2 c.c.) of concentrated nitric acid, and the solution is diluted to a suitable volume to give a strength of about 0·1 *N*; solutions as strong as 2 *N* may be used, but the mercury deposited is darker and more porous; dilute nitric acid solutions of mercury salts may also be used. An aliquot part of the solution is electrolysed by means of an apparatus adapted from that of Stock and Lux (*Z. angew. Chem.*, 1931, **44**, 200). The electrolysis is carried out in a narrow beaker having a capacity 8 to 20 c.c.; the mercury is deposited on the cathode, which is made of gold wire, 6 to 8 cm. long and 0·3 mm. thick, weighing 0·1 to 0·15 grm., whilst the anode is a small platinum spiral. The beaker is covered with a moist cover-glass to prevent loss by splashing. The potential should be 3 volts and the current is 0·015 to 0·080 amp., according to the acidity. The gas developed stirs the liquid. With a current of 0·25 amp. at room temperature electrolysis for at least 15 hours is necessary. When deposition is complete the cathode is removed without interrupting the current, washed by immersion in water, dried either for 3 hours over phosphorus pentoxide or for 24 hours over asbestos soaked in sulphuric acid, and weighed. For weights exceeding 0·9 mgrm. a longer cathode, twisted into a spiral, should be used. The cathode is cleaned by heating it over a very small flame. J. W. B.

Micro-Determination of Mercury. V. Majer. (*Mikrochem.*, 1932, **11**, 21–30.)—Mercury in amounts varying from 0·014 to 0·0001 mgrm. in a volume of 5 c.c. is determined by electrolysis. From a number of determinations of the amount of mercury left in solution after varying intervals of time, the deposition of mercury was found to follow a regular rule:—$\log s = \log s_0 - 0{\cdot}434\,Kt$, where s_0 is the original concentration of mercury in solution, and s that after time t. The constant, K, depends on temperature, rate of stirring, and surface of the vessel, and, in the conditions of the experiment, was found to be $4{\cdot}9 \times 10^{-2}$ min.$^{-1}$, and the deposition was 99 per cent. complete in 94 minutes, the temperature being 50° to 60° C. *Detail.*—The electrolysis-vessel consists of a test-tube, 110 mm. long and 8 to 8·5 mm. in diameter; this contains about 5 c.c. of solution (0·5 grm. of potassium chloride, mercury as mercuric chloride, one drop of approximately saturated ferrous sulphate solution, 0·1 c.c. of 0·5 per cent. copper sulphate solution, and two drops of 1 *N* sulphuric acid). The test-tube is immersed in a bath of known temperature, and the solution is stirred by small bubbles of carbon dioxide from a fine capillary dipping in the liquid; the carbon dioxide also prevents atmospheric oxidation. The mercury is deposited on a clean piece of iron wire, 110 mm. long, 0·4 mm. in diameter, placed in the solution. When chlorine is present in the test-solution, after the addition of 0·5 grm. of potassium chloride, clean air is passed through for 10 minutes; this removes all but about 10 per cent. of the chlorine, the last traces being removed by the ferrous sulphate. Sulphuric acid and copper sulphate, as before, are added, and the further procedure is the same; the iron wire is changed after each 30 minutes, and a further micro drop of copper sulphate is added. A total volume of up to 20 c.c. instead of 5 c.c. may be used, containing the same amount of mercury, but the constant K is then somewhat smaller. The weight of mercury deposited is calculated from the size of the drops of mercury distilled off from the iron wire. The wire is first dried for 15 minutes over phosphorus pentoxide, and is placed in a small distillation-tube drawn out to a capillary, 8 cm. long and less than 0·1 mm. in internal diameter. After distillation and centrifuging in alcohol the mercury usually forms a single drop which can easily be measured under the microscope. When several drops are formed it is necessary to place a cover-slip, etched with a numbered net-work (similar to Jörgensen's cover-slips) on the slide, so that the drops of mercury can be located and not confused with each other; they can be identified at 130 × magnification, and may be measured at 360 × magnification. The method has been used for the determination of mercury in the atmosphere.

J. W. B.

Rapid Determination of Small Amounts of Thallium in the Presence of Lead and Bismuth. F. Pavelka and H. Morth. (*Mikrochem.*, 1932, **11**, 30–33.)—A nephelometric method is used for the determination of amounts between 0·05 and 0·02 mgrm. of thallium; as much as 30 times the amount of bismuth and 50 times the amount of lead do not interfere; results are obtained with an error of the order of 2 or 3 per cent. *Detail.*—The test solution, which should contain 20 to 100γ of thallium per c.c., is treated with 2 or 3 drops of 1 : 1 nitric acid and 2 to 4 drops of 5 per cent. phosphomolybdic acid solution. After the liquid has stood for 5 minutes, and has been diluted to a suitable volume, such as 10 c.c., the turbidity is compared with that of a standard solution of thallium nitrate, containing 50 mgrms. of thallium per litre, which has been treated in the same way. The turbid precipitate formed cannot be filtered or centrifuged. Neither lead, bismuth, mercuric nor cadmium salts react with the reagent, but mercurous salts give a precipitate in dilute solutions of nitric acid, which dissolves on addition of further nitric acid. Potassium and ammonium salts should not be present. The turbidities were compared in an Autenrieth colorimeter; a Hahn colorimeter would also be suitable.

J. W. B.

Micro-Detection of Aluminium. F. L. Hahn. (*Mikrochem.*, 1932, **11**, 33–36.)—The test for aluminium with 1,2,5,8-tetra-hydroxy-anthraquinone (quinalizarin) is more sensitive when carried out as a spot test than in a test-tube. The reagent reacts with magnesium in sodium hydroxide solution, giving a coloured precipitate. Beryllium can be precipitated from this solution in the presence of ammonium salts, whilst aluminium is precipitated in slightly acid solutions (p_H = 5·4 to 5·8), so that magnesium does not interfere with the test. *Detail.*—Ten mgrms. of quinalizarin are dissolved in 2 c.c. of pyridine and diluted with

20 c.c. of acetone. Filter paper is treated with this solution and dried. The paper has the same lilac colour as light litmus paper, and turns red with acid and blue with alkali. When a drop of aluminium solution is placed on the paper the fleck appears bluer when held over ammonia, and redder when held over glacial acetic acid, than the surrounding paper. For aluminium alone the smallest amount detectable is $5 \times 10^{-3}\gamma$, and the limit of dilution is 5×10^{-7}. In the presence of 50,000 times the concentration of magnesium 1γ of aluminium in 1 c.c. can be detected.

J. W. B.

Reviews.

THE BRITISH PHARMACOPOEIA, 1932. Published by Authority, under the Direction of the General Council of Medical Education and Registration of the United Kingdom. Pp. 50+713. London: Constable & Co., Ltd., 10–12, Orange Street, Leicester Square, W.C.2. September 30th, 1932. Price 21s. net.

A new Pharmacopoeia is often approached with mixed feelings, the hope that all the shortcomings of the previous edition will have been made good being coupled with the knowledge that an intimacy arising out of many years' companionship will be suddenly broken. The publishers have, however, done their best to create a most favourable first impression by the style in which they have issued the work, and the use of water-proof cloth for the cover will be a very great advantage in the case of a book which is destined for frequent use in the laboratory. The principal change in the format of the work is the use of small type for the characters and tests in the monographs; this change would appear to have been necessary to keep the work within reasonable dimensions, as it already runs to over 760 pages—an increase of 127 pages over the number in the revision of 1914.

The present revision of the Pharmacopoeia differs from its predecessors in that it has been prepared under the direction of a body, appointed by the General Medical Council on the advice of its Selection Committee, styled the Pharmacopoeia Commission, the general supervision of the work still being carried out by the Pharmacopoeia Committee of the General Medical Council. It was decided that the Commission should consist of a Chairman, three medical men, a pharmacognosist, a pharmacist, and an analytical chemist, together with a secretary. The actual work of sifting the mass of information available was carried out by six sub-committees appointed by the Commission, which sub-committees have in addition carried out a vast amount of work in deciding upon the most suitable tests and standards to be adopted. It is difficult to criticise seriously the constitution of these committees, consisting, as they do, entirely of those long and honourably known in their respective spheres; the addition of at least one other Public Analyst to the Pharmaceutical Chemistry Sub-Committee, however, might well be considered in the future.

The Pharmacopoeia Commission has attempted to produce a volume suitable for the whole British Commonwealth of Nations, but it has not included substances which have mainly a local use in particular parts of the Empire, as was done in the 1914 revision. It is anticipated that supplementary lists of substances may be issued under local laws in the particular parts of the Empire to which they refer. There is a precautionary legal note pointing out that in some parts of the Empire the Pharmacopoeia has statutory force, and also that there are local laws dealing with certain of the substances which are the subject of the monographs; an attempt has been made to mention all such cases, but it is to be understood that any direction of the Pharmacopoeia which is contradictory, or inconsistent with, the local law is deemed thereby to be superseded. It is hoped to publish complete future revisions at intervals of ten years, but it may be found expedient to issue supplements from time to time during the intervals of revision.

The International Agreement of 1930, to which His Majesty's Government subscribed with certain reservations, has been carefully considered during the compilation of the revised Pharmacopoeia. Of the 76 articles contained in the Agreement, 43 have been included in the Pharmacopoeia. Of these, 25 are in accord, whilst 18 differ in composition or strength. Of the 18, two are standardised on a different basis, 9 for which there are no standards in the Agreement are standardised in the Pharmacopoeia, whilst for 7 the standards given in the Pharmacopoeia differ, varying from half the amount in the Agreement (in four cases) to twice (in one case). With regard to the main general alterations which have taken place as a result of the present revision, it will be found that the list of additions comprises 128 articles, and the list of omissions 357 articles, whilst there are also 113 articles of which the names have been altered, 18 of which the composition has been altered, and 13 of which the strength has been altered.

It is reported that an arrangement has been made with the Pharmaceutical Society of Great Britain for all the omissions from the 1932 revision of the Pharmacopoeia to be described in the next edition of the British Pharmaceutical Codex.

Many preparations have been omitted on the score of redundancy or lack of therapeutic value. They are not considered further in this note, as the point is one of medical rather than analytical interest, but the following sentence from the Introduction is deemed of sufficient interest to quote: "The mere fact that a drug is frequently prescribed has not been a sufficient justification for its inclusion, and a number of drugs described in the last British Pharmacopoeia have been omitted on the ground of insufficient medicinal value." With regard to the question of the position of the Pharmacopoeia as a legal standard under the Food and Drugs (Adulteration) Act, the following quotation from "General Notices" is also of interest: "Substances or preparations so designated" (*i.e.* having the official titles as descriptions) "for use in medicine must conform to the requirements of the British Pharmacopoeia."

Molecular weights have been added for the first time; these are calculated to the first decimal place in most cases, although that of water is taken to the third. We are told that "The Tests for Identity are provided only as an aid to identification; they do not in every case suffice to establish proof of identity," but no indication is given as to whether this is due to the limitations of the present knowledge of analytical chemistry or to a desire to keep the monographs short.

The former of these alternatives is difficult to believe, and the latter would represent an undesirable state of affairs, as the obvious use of "Tests for Identity" is to identify the substance in question.

The general tests given in the appendix have been increased in number, and illustrations appear for the first time in the Pharmacopoeia. Some of the Qualitative Reactions given in Appendix V could have been extended with advantage. Thus the evolution of ammonia is to be recognised by the odour only, but the effect on litmus is much more sensitive, particularly to certain individuals. None of the various modifications of Denigès' test is given; neither is the persulphate test, nor the cobaltinitrite test for potassium, and there is no mention of any of the newer tests for the metals with organic precipitants. Many of these are specific and all are valuable, particularly as micro-methods.

The quantitative test for lead remains substantially the same, although the permissible limits have, in many cases, been reduced. The solutions to be tested are still directed to be filtered while alkaline, but in this case in the presence of ammonium acetate, since acetic acid is first added and subsequently neutralised by the addition of ammonia. The ammonium acetate appears to prevent that adsorption of lead on the filter paper, which takes place when alkaline solutions of lead are filtered. The method has been tried in the reviewer's laboratory with satisfactory results. The quantitative test for arsenic is also little changed, but the method of attaching the mercuric chloride paper is much improved. Many of the limits have been considerably reduced, and it is interesting to observe that in some cases, *e.g.* citric and tartaric acids and glucose, the limits given are lower than the one-hundredth of a grain per lb. (1·4 part per million) suggested by the Royal Commission on Arsenical Poisoning.

In addition to the tests for lead and arsenic, there are quantitative limit tests for chlorides, sulphates and iron. The addition of these tests is typical of the alterations made in connection with the tests for purity, which are generally more precisely defined. The phrase in the 1914 revision "shall not answer for the tests for . . ." no longer occurs, and in its place definite tests limiting the permissible amounts of impurities are laid down. In the determination of water-soluble ash, although it is directed that the ash shall be boiled with 25 ml. of water, the volume of the washing water is not specified. In ashes containing such salts as calcium sulphate the results obtained depend very largely on the amount of wash water used.

The strengths of many of the preparations (*e.g.* the acids and alkalis) are still given exactly, but the permissible limits are given in brackets immediately following. Thus acetic acid is stated to contain 33 per cent. w/w of real acid within the limits of 32·5 to 33·5. This is a great improvement and should do much to remove many uncertainties which have arisen in the past.

The description "Absolute alcohol" has been changed to "Dehydrated alcohol." To "dehydrate" surely means to deprive of water, and, as the strongest commercial alcohol is never either "absolute" or "deprived of water" in the limiting sense, there hardly seems sufficient reason to change such a well-known name.

The descriptions of some of the crude drugs are, at first sight, a little ambiguous. Thus, under Buchu, we find "It contains not more than 5 per cent. of the stems, and not more than 2 per cent. of other organic matter." Presumably what is meant is that 93 per cent. of the sample shall consist of Buchu leaves, but the use of the term "other organic matter" in this and other monographs appears to the reviewer to be rather unfortunate.

Alum, Borax and Cream of Tartar no longer have the prefix "purified," but there is a notice to the effect that the standards of the Pharmacopoeia do not necessarily apply to articles which are sold, under the same name, for other than medicinal use. This is a great improvement. Any Food and Drugs Inspector asking for "Purified Borax" immediately advertises his office, and yet there was always a difficulty in applying the Pharmacopoeial standards unless the exact Pharmacopoeial names had been used when purchasing.

Ergot is now standardised by means of the Van Urk-Smith colorimetric method. There are only two preparations—prepared ergot, which is powdered de-fatted ergot, and the liquid extract—both of which are standardised in a similar manner. It has, of course, been known for some years that the ergot preparations of the 1914 revision are valueless. There seems to be every reason to expect that this difficulty has definitely been overcome. No biological methods for the standardisation of ergot are suggested, although biological methods of standardisation are an important new feature of the work, these following, wherever possible, the Regulations made under the Therapeutic Substances Act, 1925.

Although many concentrated preparations have been on the market for a number of years, they have not previously been admitted to the Pharmacopoeia. On this occasion, however, eight concentrated infusions are described. There is, however, no concentrated infusion of digitalis, and it is expressly stated that for dispensing purposes fresh infusion of digitalis should be used, and this within twelve hours of its preparation.

The oil in crushed linseed is directed to be determined by extraction with ether. Petroleum spirit is now more usual.

Some preparations (*e.g.* solutions of ammonium acetate) are directed to be prepared to a given p_H, full directions for a suitable colorimetric process being given in one of the Appendices.

Interesting additions are such names as Lysol, Formalin and Aspirin, with the reservation that their use is limited to Great Britain and Northern Ireland, and that in those parts of the Empire where they are trade-marks they may be used only when applied to the products of the owners of the trade-marks.

The familiar specific gravity of ether (0·720) has now been altered to 0·720–0·724, which is probably more accurate, in spite of its unfamiliar appearance.

The names of the alcoholic solutions of simple substances have been altered from tinctures to liquors in accordance with the International agreement, although the former names are retained as synonyms; iodine and ammoniated quinine are popular examples. The medicated wines have all been omitted in accordance with the International Agreement. Ipecacuanha wine is replaced by a tincture of ipecacuanha having the same proportion of alkaloids. A slip inserted states that the tincture should be given in cases where the wine is called for, which suggests the possibility of the raising of some slight legal difficulties under the Food and Drugs (Adulteration) Act. Industrial methylated spirit is at last introduced, and is used in the preparation of 15 compounded articles, apart from its use in many instances in the preparation of reagents.

No material alteration is made in the names of magnesium oxide and magnesium carbonate, the former still being described as magnesia. Gregory's Powder, however, is now made from the carbonate, and not from the oxide, as formerly.

There is no question but that greater advances have been made and a greater number of improvements added than in any previous revision. All those who have given so freely of their time and their experience to the production of such a work are to be warmly thanked and heartily congratulated. The amount of work involved in the revision must have been enormous, but is justified by the results obtained. To all those either directly or indirectly interested in drugs, the work is, of course, indispensable, but every analyst will find it is of very great value as a work of reference in many different fields.

G. D. ELSDON

THE B.D.H. GUIDE TO THE B.P., 1932. Pp. xvi+122. London: The British Drug Houses, Ltd., Graham Street, City Road, N.1. 1932. Price 2s. 6d.

This volume can be heartily recommended as a handy and most useful guide to the 1932 revision of the British Pharmacopoeia. It is well printed on good paper and nicely bound in dark blue cloth, the only improvement that can be suggested in its general appearance being that its length might have been increased by about a quarter of an inch to make it uniform with the Pharmacopoeia itself.

The book consists of two parts: First, an introduction describing the main lines of difference between this revision and its forerunners; and, secondly, more detailed notes on each of the monographs now official. The plan has been adopted of placing a double black line at the extreme left hand of each note dealing with a substance which has been altered to a material extent, and a single black line against any note dealing with a substance which becomes official for the first time.

A vast amount of information has been condensed in an admirable manner, the minor alterations in purity or strength being all clearly expressed. The book cannot, of course, be used in any way as a substitute for the Pharmacopoeia; the intention of the publishers is that it should be used along with the new revision to facilitate comparison with the old; this rôle it will admirably fulfil.

G. D. ELSDON

CHEMICAL ENCYCLOPAEDIA. By C. T. KINGZETT, F.I.C. Fifth edition. Pp. viii+1014. London: Baillière, Tindall & Cox. 1932. Price 40s.

The demand for a volume of this description is evident from the fact that five editions have been published during the last thirteen years, and, in spite of rigorous condensation, the present one contains over 200 pages more than the previous edition. The text comprises a series of definitions and brief articles on a multitudinous selection of chemical subjects arranged in alphabetical order with, in many cases, references to scientific publications where further information may be obtained. Not only are the purely chemical terms for substances given, but also many trade names, and the author has wisely included references to some of the commoner physical phenomena. On the other hand, a small number of the subjects, such as "Labour in Industry," appear somewhat out of place in a work of this nature.

It would be impossible, in reviewing this volume, to check the whole of the data and references given, but an extensive investigation has failed to detect any error, either numerical or typographical, and the statements of fact are free from the serious errors too often encountered.

The whole volume is well produced, with legible text and excellent binding, and reflects great credit upon the author, whose patient and careful work has produced a work which will undoubtedly be in extensive demand and of considerable value to a wide circle of readers.

T. J. WARD

MAKERS OF CHEMISTRY. By ERIC JOHN HOLMYARD. Pp. xvi+314. Oxford: Clarendon Press. 1931. Price 7s. 6d. net.

If the justification of an author lie, as Sidney says of poetry, in his ability "to teach and to delight," then Dr. Holmyard, for one, has more than fulfilled his duty to his readers. In his latest book in the *Makers of Science* series he delightfully combines the two arts, so that our minds receive both entertainment and instruction at the same time. A skilful lapidary, he has culled the gems from many an ancient treasure-store, polished and cut them to his taste, and then displayed them anew in a setting of his own making. *Makers of Chemistry* is filled with data and anecdote nicely blended, which bear ample witness to the laborious and painstaking hours of study put in by the author. Primarily intended for the non-scientific reader, the book is written in a simple, lucid style that all may understand, with that happy choice of words for which Dr. Holmyard has become so justly famed. Insensibly the layman becomes interested in the chemical phenomena until, by the time the end is reached, he finds himself thinking in terms of chemistry. The book should prove a great boon to the average student of chemistry who does not wish to spend much time delving into many sources for a history of the subject, for here, clearly and concisely set out, is all he needs to know of the general lines of its development, "from its remote and obscure beginnings up to the establishment of the modern science by Dalton, Lavoisier, Avogadro, and their contemporaries." A special word of praise is due for the well-chosen illustrations, of which there are close on a hundred, of great interest in themselves.

Dr. Holmyard may congratulate himself on having admirably achieved his purpose, to enable "those with no special scientific training to understand how the great and fascinating science of chemistry slowly took shape, until at length it was set firmly upon its present fruitful course." *Makers of Chemistry* can but enhance the author's reputation, already widespread and always growing, as a writer of readable books.

M. NIERENSTEIN

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